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A METHOD OF DETERMINING THE DETERGENT ACTION OF SOAPS

BY J. W. McBAIN, R. S. HARBORNE AND A. MILLICENT KING

In spite of the many investigations on the subject of detergent action[1], there is still no recognised standard in terms of which the washing power of soaps can be expressed. This communication describes quantitative measurements of detergent action upon one substance: namely, carbon black.

Striking, although only qualitative, experiments describing the action of solutions of a "medicinal soap" in suspending lamp black were published by Spring[2]. He found an optimum effect in one per cent solution and even in dry methyl and ethyl alcohols there was an optimum concentration although in very much more dilute solution. He even found that dilute aqueous soap solutions had the power of carrying a certain portion of the lamp black through a filter paper although this did not occur when using alcohol.

Spring concluded that a sorption compound was formed between the lamp black and the soap or rather (upon somewhat doubtful evidence) between lamp black and somewhat acid soap. The suspended lamp black passed through filter paper without blacking it although, in the absence of soap, none passed through, and the black clung tenaciously to the paper. Spring's conception of detergent action is therefore represented by an equation of the form

$$\text{Fabric}\cdot\text{dirt}+\text{soap}=\text{fabric}+\text{dirt}\cdot\text{soap}$$

McBain[3] proposed the more logical alternative of double decomposition; namely,

$$\text{Fabric}\cdot\text{dirt}+\text{soap}=\text{fabric}\cdot\text{dirt}+\text{soap}\cdot\text{dirt}$$

for which there is a good deal of evidence.

In Spring's experiments with lamp black and in ours with carbon black only a portion of the carbon, that stably suspended, is carried through the filter paper. We utilise this fact and simply determine the amount of carbon black carried through. The "carbon number" of a soap solution is the number of grams of carbon carried through by one kilogram of soap solution under standard conditions.

Preliminary Experiments by R. A. W. Bond

Much time was spent by Mr. R. A. W. Bond in studying various samples of lamp black and carbon black. That which gave the largest effect was "Auk" carbon black, a 15 lb. sample of which was supplied through the kindness of Messrs. Chance and Hunt of London. Their "Kalista" carbon black was only slightly less effective.

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[1] Cf. McBain: Third Colloid Report of the Brit. Ass. Adv. Sci. p. 24 (1920)

[2] Kolloid-Z. 4, 164; Rec. Trav. chim. 28, 120 (1909)

[3] Loc. cit.

Extraction of the carbon black with ether in a Soxhlet apparatus was detrimental owing to the agglomeration of the carbon; hence in all further work untreated original carbon black was employed.

Twenty ccs. of soap solution carried through most carbon when shaken with one gm. of carbon black, this amount being more effective than either 2 or 0.5 gms., thus in experiments with No. 5 Whatman filter papers and 0.1N_w potassium myristate the carbon numbers found were 0.56, 0.33 and 0.11. No explanation is afforded.

A large number of filter papers were tested and No. 31 Whatman Filter Paper was finally adopted as being most porous and yet fairly uniform. For the gravimetric analysis of the filtrate the only satisfactory paper was No. 590 Schleicher and Schüll filter paper.

Time of exposure of the lamp black to the soap was varied from one day to one month without noticeable effect. Increase of temperature greatly diminished the carbon number. It was found in accordance with expectation that there was an optimum concentration of soap solution.

Experimental

Materials.

Only soaps prepared from pure fatty acids were used, the potassium oleate was prepared by Kahlbaum and contained three equivalents per cent excess acid. Other soap solutions were prepared, with the precautions described by Bunbury and Martin[1], from pure fatty acids supplied by Kahlbaum but using Jena glass vessels with well vaselined glass stoppers. The importance of the last precaution which is invariably adopted in this laboratory is strikingly illustrated by the following Table I.

TABLE I

Acidities of Potassium Oleate Solutions in Equivalents of Free Acid to 100 Equivalents of Soap

Description of solutions.	Stopper employed	Acidity. When fresh.	Acidity. Next day.
Soap dissolved in 2 parts alcohol + 1 part water.			
Sample I.	Unvaselined glass.	2.87	4.11
Sample II.	Vaselined glass.	2.89	2.93
0.05N_w aqueous soln. + 2 parts alcohol.	Well vaselined cork.	7.67	16.36
0.496N_w aqueous soln. + 2 parts alcohol.	Well vaselined glass.	3.27	3.34

---

[1] J. Chem. Soc. 105, 417 (1914)

Increase in acidity is due chiefly to entrance of carbon dioxide but partly to oxidation. Distilled water and alcohol were always boiled out in a pyrex flask. The acidimetric standard was benzoic acid supplied by the Bureau of Standards Washington and constant boiling hydrochloric acid prepared by the method of Hulett and Bonner. The great importance of exact neutrality is shown by the sequel. As far as possible dilute solutions were prepared by direct dilution of more concentrated stock solution but a large number of independent solutions was also made up.

Procedure.

In determining the amount of carbon carried through a filter paper by soap solution the following standard method was adhered to. One gram of "Auk" carbon black weighed within 1% was placed in a large test tube with 20 ccs. of the soap solution, shaken thoroughly and allowed to stand for 23 hours in a thermostat at the experimental temperature, shaken again and allowed to stand a further hour before being poured upon an 11.3 cm. No. 31 Whatman filter paper. The filtration was also carried out in the same thermostat (a water-jacketed copper chest kept within 0.5°) and allowed to stand until approximately 10cc. of filtrate had collected. The filtrates were then analysed either by the gravimetric or in all later work the colorimetric method. The data given in the present paper enable absolute results to be readily obtained in other laboratories by simple camparison with ours.

Gravimetric method of analysis.

The carbon in the filtrate had to be isolated and weighed on a filter paper. A 5.5 cm. 590 Schleicher and Schull filter paper which had previously been extracted with alcohol in a Soxhlet extractor was dried at 110°C in an electric oven for 45 minutes. It was then transferred quickly to a small weighing bottle fitted with an air tight stopper. The filter paper was then weighed by difference and the drying repeated until the weight (about 0.12 g.) remained constant to 0.1 mg. It was then necessary to obtain on this dried analysis filter paper the whole of the carbon in the filtrate. Two methods were adopted depending on whether the concentration of the soap was greater than or less than 0.3N. In the latter case, the carbon suspension (i.e. the filtrate) was decomposed by the addition of about 20 cc. of alcohol and then filtered through the analysis paper, the whole of the carbon being retained without difficulty. The carbon was then thoroughly washed free from soap with hot alcohol. When the concentration of the soap solution was above 0.3 N, it was found that so much alcohol was required to break the suspension and dissolve the soap that the time taken to filter this large bulk of liquid was too long for the first method to be employed.

In the second method, the suspension was decomposed by the addition of a few ccs. of dilute sulphuric acid (approx. 0.5N). The water was then decanted, through the analysis filter paper, from the fatty acid precipitate formed and the latter melted by warming to about 60°C., and then poured on to the filter paper. The tube and filter paper were then washed free from fatty acid by means of hot alcohol, the carbon being retained on the filter paper.

The alcoholic washings were tested for fatty acid by dilution with cold water, a white ring of myristic acid precipitate being formed if not free from fatty acid. This washing operation had to be carried out with great thoroughness otherwise misleading high results were obtained.

The filter paper and carbon thus obtained were then dried in the electric oven and weighed under conditions as far as possible identical with the previous drying and weighing, i.e. dried at 100° for 45 mins. and weighed in an air-tight weighing bottle. The increase in weight gives the weight of carbon in a known weight of filtrate, which is then expressed in "carbon numbers", grams carbon per 1 kilo soap solution.

This method of analysis is restricted in use, although essential for obtaining an absolute standard for all subsequent work. In the first place, the limit of weighing on an ordinary chemical balance gives a possible error in the carbon number of about 10% for a 0.1N solution when only 10 grams of filtrate are taken. If more than 10 gms. of filtrate are taken the bulk of the liquid becomes great, thus making the process of filtering off the carbon from the decomposed filtrate very long and tedious. Moreover, as the amount of carbon on the analysis filter paper increases beyond ten milligrams, the time taken to wash free from acid or soap is so long that the probability of error from incomplete washing overwhelms the advantage of having a comparatively large amount of carbon on the filter paper.

It is therefore seen that the gravimetric method may only be used with advantage with such concentrations of soap solutions as give a carbon number of about 0.5 to 1.0 unless a micro balance accurate to within 0.01 mgs. is used.

Colorimetric method of analysis.

In this method the filtrates (about 10 gms. in every case) were diluted to known volume by the addition of a large excess of alcohol. For the sake of convenience, these diluted filtrates are termed "test filtrates". A convenient concentration was obtained by weighing out accurately about 1 gm. of filtrate and diluting to 100 ccs. with alcohol, the solution being well shaken and allowed to stand for a few minutes before being analysed in order that the alcohol might dissolve the soap. The length of column required to give the same transmission of light as a column of standard test filtrate was then ascertained by means of a colorimeter. According to Beer's Law, the amounts of carbon in the two test filtrates are inversely proportional to the length of the columns giving the same transmission of light. Thus the concentration of the filtrates can quickly be compared with that of the standard filtrates. A Donnan colorimeter was used but less accurate comparisons could be made by eye.

The carbon number of the filtrate is given by the formula

$$C = \frac{l_s w_s}{l_w} \cdot C_s = 0.54 \frac{l_s w_s}{l_w}$$

where l_s and l_w are the lengths of the columns of standard liquid and filtrate respectively and w_s and w are the weights of standard and of filtrate which have been diluted up to 100 cc. with alcohol.

The filtrate from $0.125N_w$ potassium myristate was arbitrarily chosen for the standard test filtrates because the value of the carbon number had been carefully established for this case by the gravimetric method of analysis as 0.54 ± 0.01.

The final step towards simplifying the manipulation and rendering it possible for other laboratories to obtain results in our units was made by replacing the standard filtrate by a dye solution of similar colour prepared from pure dyes obtained from British Drug Houses Ltd. The specification of this standard was:
20 cc. Nigrosine solution of concn. 0.056 gm. per litre.
20 cc. Bismarck Brown soln, of concn. 0.0858 gm. per litre.
100 cc. distilled water.

This dye solution was found equivalent in light transmission to a test filtrate of carbon number 1.19. The carbon number value of 1.19 was the absolute value obtained by comparing the dye standard in the colorimeter with test filtrates prepared from filtrates which had been analysed gravimetrically. This dye standard, which is quickly prepared and easily reproducible possesses many advantages as a standard over any filtrate, which is not only subject to a greater experimental error in preparation but also liable to error due to occasional non uniformity of the filter papers.

Hence to obtain the carbon number of any commercial soap, using a sample of our carbon black, it is only necessary to compare the filtrate (after diluting w gms. to 100 cc. with alcohol) with the standard dye solution and apply the formula

$$C = 1.19 \frac{l_s}{l_w}$$

We are prepared to supply small samples of our carbon black for purposes of standardising the stock used by other investigators. Or, the same result can be obtained quite independently by carefully preparing any of the soap solutions whose carbon numbers are properly recorded in this paper and standardising the carbon black or other carbon therewith; it is only necessary to determine with that soap solution, the ratio between the depth of colour of the filtrate obtained and the colour here recorded to have a constant factor which will convert all experimental results using commercial soaps with any definite kind of carbon or lamp black into the standard units of carbon number.

Experimental Results

Concentrations of soap are expressed in per cent i.e. gms. of soap in 100 gms. of solution, as well as in weight normality (N_w), that is, gram equivalents of soap in 1 kilogram of water.

Table II contains the data for various concentrations for pure potassium myristate at temperatures between 12 to 15°C. Each value is the mean of a large number of determinations.

Tables III and IV exhibit the important influence of very slight additions of either free alkali or free fatty acid. Table V shows the effect of change of temperature. Table VI gives the results for various concentrations of potassium oleate and here the filter paper was folded by gentle pressure between finger and thumb since it had been found by Messrs. Allnutt[1] that increased pressure may cause slower filtration and give inconsistent results.

TABLE II. (see graph I.)

Variation of Carbon Number with Concentration of Solutions of Neutral Potassium Myristate.

Soap.		Mean carbon numbers.	
%	N_w	Gravimetric (12 to 15°)	Colorimetric 12° to
0.268	0.01		0.03
0.662	0.025		0.10
1.32	0.05	0.17	0.21
1.96	0.075	(0.47)	0.32
2.59	0.10	0.49	0.41
3.22	0.125	0.54 ± 0.01	0.54*
3.84	0.150		1.28
4.45	0.175		2.18
5.06	0.20		0.40
6.24	0.25		0.35
7.40	0.30	0.29	0.30
9.63	0.40		0.22
13.8	0.60		0.025
18.0	0.80		0.01

*Indicates standard upon which all colorimetric readings are based.

TABLE III. (see graph II. right hand portion)

Carbon Numbers of Potassium Myristate plus excess of KOH.

Soap.		Excess of KOH		Temp.	Carbon
%	N_w	N_w	Equivalents %	°C.	number.
3.22%	$0.125N_w$	$0.000N_w$		15	0.54
"	"	0.00125	1	16	1.27
"	"	0.00625	5	16	2.06
"	"	0.0125	10	16	3.98
"	"	0.0218	15	14	2.83
"	"	0.0250	20	16	3.02
"	"	0.0375	30	14	4.09
"	"	0.0500	40	13.5	5.60
"	"	0.0625	50	13.5	10.0
"	"	0.0750	60	14	3.52
"	"	0.0875	70	14	4.22
"	"	0.125	100	13	3.58
"	"	0.250	200	13	1.23
"	"	0.375	300	13	0.83
"	"	0.625	500	13	0.27
4.45%	$0.175N_w$	$0.00875N_w$	5%	11.5	0.65
"	"	0.0175	10	11.5	2.60
"	"		15	15.0	7.38
"	"		30	11.9	6.7
"	"		50	11.5	6.25
"	"	0.176	100	11.5	3.16

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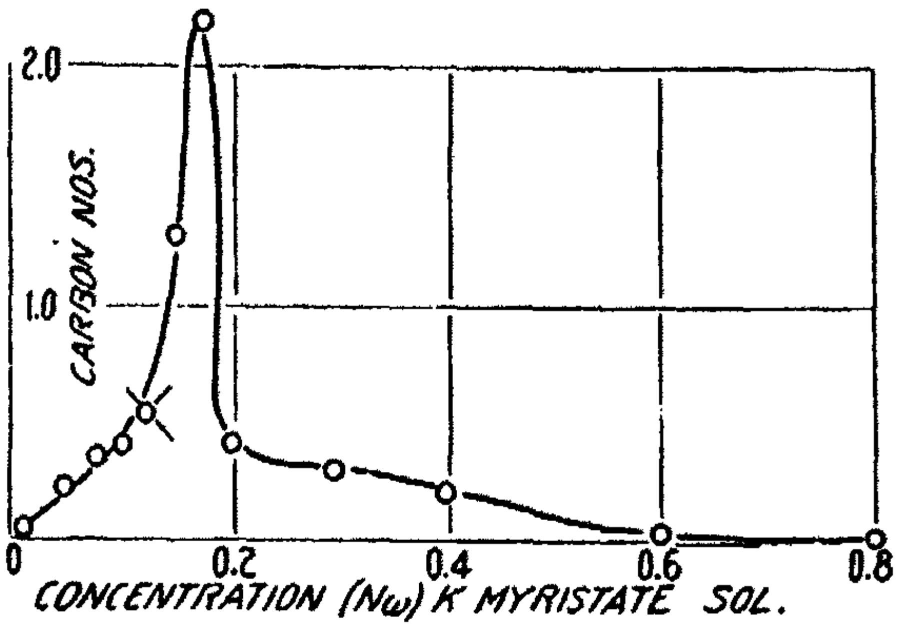
[1] J. Soc. Chem. Ind. 42, 565 (1923)



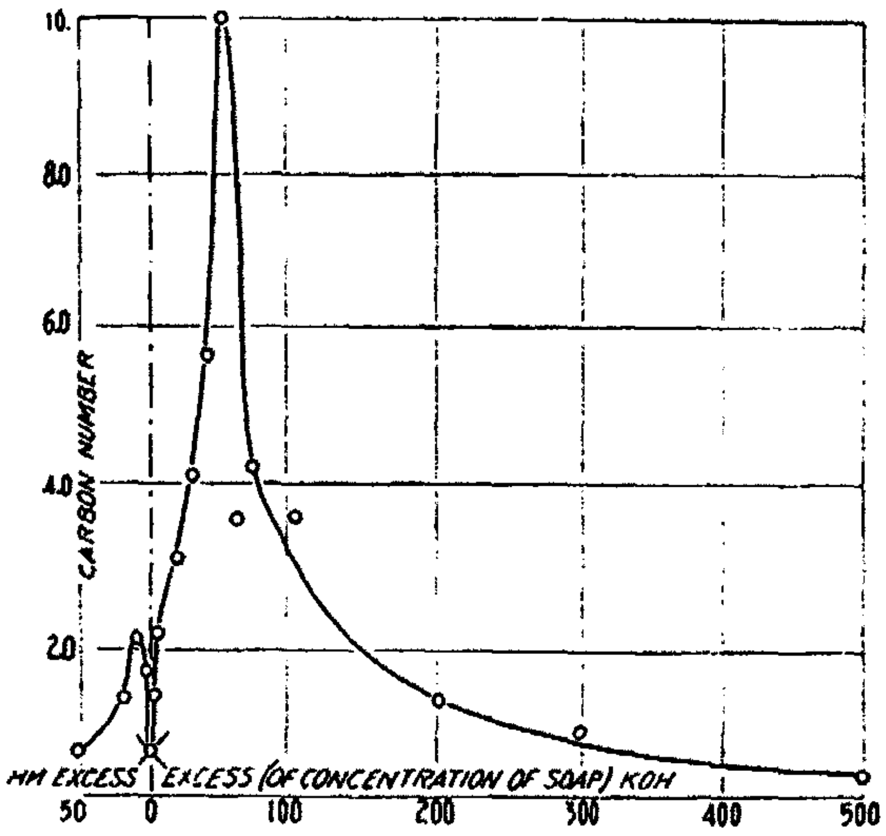
Graph I

Variation of Carbon Number with Concentration of Solutions of Potassium Myristate (Neutral)

TABLE IV. (see graph II, left hand portion)

Carbon Numbers of $0.125 N_w$ ($= 3.22\%$) Potassium Myristate Solution plus excess of Myristic Acid

% (of concn. of soap) excess H Myr.	Mean C. No.	Temp. (°C)
0	0.54	15
1	1.6	12
5	1.9	12
10	2.0	11
20	1.21	11
50	0.58	11



Graph II

Variation of Carbon Number of 0.125 Nw K. Myristate Solution with excess Myrstic Acid (HM) and excess KOH. The cross is neutral 0.125 Nw soap corresponding to the cross in Graph I.

TABLE V.

Variation of Carbon Number of Pure Neutral 0.1N_w (=2.59%) Potassium Myristate with Temperature.

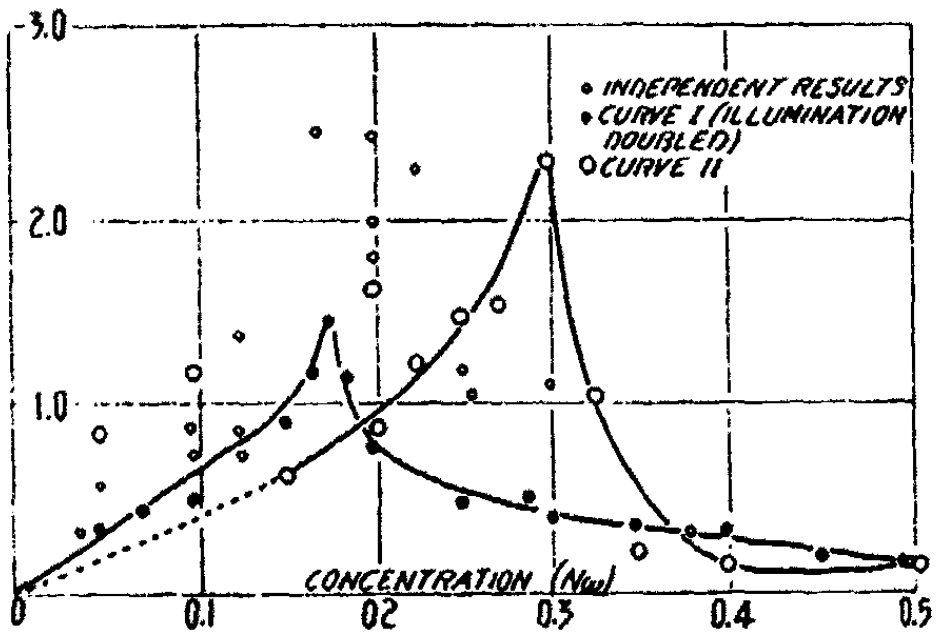
Temperature	11.5°	15°	25°	60°
Carbon Number	0.51	0.41	0.22	0.15

TABLE VI. (see graph III).

Variation of Carbon Number of Solutions of Potassium Oleate with Concentration.

Soap.		Independent	Results.	Curve I*.		Curve II.	
%	N_w	Temp.	C. No.	Temp.	C. No.	Temp.	C. No.
19.8%	0.77N_w	12.0°	1.29°				
13.9	0.503					20.5°	0.12
12.9	0.495	12.1°	0.10	13.9°	0.17	17.5°	0.11
12.6	0.450			13.9°	0.17		
11.4	0.40			13.4°	0.31	17.6°	0.13
10.9	0.38	12.5°	0.31				
10.1	0.35			13.4°	0.36	17.4°	0.21
9.44	0.325			13.3°	0.45	17.4°	1.03
8.77	0.30	14.75°	1.09	13.6°	0.39	17.5°	2.16
		13.10°	2.14			19.5°	2.27
		19.5°	2.27				
8.50	0.29			13.7°	0.51		
8.40	0.286	14.75°	1.66				
		14.50°	3.20				
7.96	0.27			13.7°	0.57	17.6°	1.53
7.50	0.253	12.8°	1.05				
7.42	0.25	11.5°	1.17	13.5°	0.47	17.8°	1.33
6.73	0.225	12.50°	2.24			18.6°	1.21
6.02	0.20	12.55°	3.53	13.6°	0.77	18.6°	0.82
		13.45°	2.42			19.8°	1.60
		14.5°	1.78			20.7°	0.87
		19.4°	1.96				
5.60	0.185			13.9°	1.14		
5.30	0.175			14.2°	1.44		
4.97	0.163			15.3°	1.15		
5.07	0.167	12.4°	2.33				
5.26	0.173			15.2°	1.23		
4.59	0.15			14.1°	0.90	19.5	0.63
3.85	0.125	11.5°	0.71	14.2°	0.83		
		14.5°	1.35				
3.11	0.10	17.5°	0.86	14.5°	0.49	17.5	0.72
2.29	0.073			14.7°	0.44		
1.58	0.05	13.7°	0.56	14.6°	.33	19.8	0.84
0.984	0.031	21.0°	0.38				
3.11	0.10	17.5°	0.52			19.4	1.17

*In the series of experiments in Curve I unsatisfactory illumination was employed in the colorimeter. Each number in Table VI. is the mean of three or four results.



Graph III

Variation of Carbon Numbers with Concentration of Potassium Oleate

Discussion of Results

It is seen from the Tables and Graphs that the results are dependent upon concentration, temperature, acidity and alkalinity.

There is a surprisingly sharp maximum carbon number at a particular concentration of soap. In the case of potassium myristate this occurs at a concentration of $0.175N_w$ ($=4.45\%$) which is a hundred times more effective than either a very dilute or concentrated soap solution. In the case of potassium oleate the existence of a similar maximum is equally obvious and it lies in only slightly higher concentration although here the effects are obscured by the great sensitiveness of oleate solutions to other external factors. It is well authenticated that there is an optimum concentration for the use of any commercial soap as a detergent. In applying this to practical washing operations it may easily be advisable to use a strong solution and to pass through the optimum concentration in the rinsing process.

The actual detergent power of the two very different soaps myristate and oleate, are unexpectedly similar although the first is derived from a saturated fatty acid containing only 14 carbon atoms whereas the other is unsaturated containing 18 carbon atoms and the oleates are regarded as soaps *par excellence*. There is no other property of soap solutions which is known to be at an absolute maximum at these concentrations, although the turbidity of such colloidal systems as soap and cellulose acetate may however pass through an ill-defined maximum at similar concentrations. There is likewise no constituent of soap solutions except possibly the hydroxyl ion which passes through a maximum of concentration in this region.

Very slight excess of either acid or alkali increases the detergent action many fold, although further excess causes it again to disappear. This is probably the chief cause in the fluctuations in the results with the oleate which so readily oxidises in the air with corresponding change in alkalinity. In the case of $0.125N_w$ (=3.22%) potassium myristate, addition of 50 equivalents per cent of alkali (=only $0.0625N_w$ KOH) increases the detergent action nineteen fold.

Temperature exhibits an important effect especially at lower temperatures where the carbon number increases very rapidly being doubled for a change of 10°. The effect is very much less at higher temperatures. It is known that the amount of colloidal soap behaves in a somewhat similar fashion.

In Graph III for solutions of potassium oleate, the two series of points connected by a continuous line represent solutions which were prepared by dilution of one sample of the most concentrated solution, the other points represent solutions made up quite independently. Miss Laing has found that solutions of sodium oleate require at least a day to attain internal equilibrium at room temperature and it is possible that even the hydrolysis alters. A direct test should be made upon the effect of time upon the detergent action of oleate solutions. Some of the erratic results were undoubtedly due to faulty filter paper since occasionally some of the carbon coming through with the filtrate settled immediately to the bottom of the test tube and a second filtration through another filter paper reduced the carbon number to the expected value.

The results with potassium oleate led to a few additional experiments which seem to show that a carbon filtrate is more effective than the original soap solution in extracting fresh carbon black and that likewise carbon black which has once been extracted produces with fresh soap solutions a filtrate of much higher carbon number than the original filtrate.

For the first experiments 8 gms. of filtrate containing carbon from a $0.173N_w$ potassium oleate solution was shaken up with a fresh quantity of 0.5 gms. of carbon and filtered through fresh filter paper. In each case the carbon number went up many fold being increased from such values as 0.76, 0.83, and 1.45 to 4.19, 4.48 and 3.09.

In the second series the carbon residues left on the filter paper from a previous filtration were treated with a fresh sample of the original soap solution to see if any further carbon could be extracted, as there was a possibility that all the fine particles had already been taken through. However the carbon number so obtained was invariably increased many fold. For instance, instead of carbon numbers 0.56, 1.14, 0.88, 1.46, 0.65 and 0.36 there were now obtained such values as 5.01, 3.59, 4.64 4.39, 5.02 and 4.57 and a third extraction with still further soap still gave quite high results.

These two results are obviously closely related since the carbon whether in the filtrate or in the residue forms a sorption compound with soap thus changing both the concentration and the composition of the solution. We have not had the opportunity of making a direct analysis of either of these quantities.

Now that a general method of making a rapid and direct test of detergent action has been set up, it should be possible, by investigating different soaps, saturated and unsaturated, pure and admixed and the effect of change of temperature, addition of salts and of excess of acid or alkali upon their detergent power to explain fully the phenomenon of cleansing action.

The action upon carbon black may be to a certain extent specific and in so far not quite parallel to the effect on oily matter, or on emulsification or on frothing but this would merely limit but not destroy the value of the direct information obtained.

Summary

A method has been developed and standardised for the direct and rapid determination of the amount of finely divided carbon which various soap solutions carry through filter paper. This gives a "carbon number" characteristic of each solution which may be taken as a measure of the detergent of this material.

It is shown that by a slight alteration of conditions the detergent action of a soap may be enormously increased. There is an optimum concentration in moderate dilution for which the effect is a maximum, very slight addition of either acid or preferably alkali greatly enhances the detergent power. Rise of temperature diminishes at first rapidly then more slowly the detergent power but this may be completely overshadowed by the vital necessity of using sufficiently high temperature to dissolve the soap. Once in solution there is surprisingly little difference between soaps as different as myristate and oleate.

In conclusion our thanks are due to the Research Fund of the Chemical Society and to the Colston Research Society of the University of Bristol for grants for the purchase of materials used.

Department of Physical Chemistry,
The University,
Bristol.

TYNDALL BLUE IN SOLIDS

BY WILDER D. BANCROFT[1]

In the spring of 1921 I noticed that a piece of capillary glass tubing lying on a laboratory desk was quite blue at the end; but was not blue by transmitted light. After some experimenting my colleague, Professor Briggs, showed that the blue color was due to the scattering of light by myriads of minute crystals embedded in the amorphous glass. If a suitable glass rod were annealed for a sufficient time at a suitable temperature, it became first blue and then white by reflected light owing to the formation and growth of crystals having a different index of refraction from the mass of the glass. When the rod was heated to a higher temperature, the color disappeared because the crystals dissolved in the hot glass.

Still better blues were obtained by Mr. Clyde Mason,[2] assistant in microchemistry, who heated a piece of hard-glass, Jena tubing in a combustion furnace at a temperature just below the softening point of the glass. Two hours of heating is generally sufficient; but the time required is shorter at higher temperatures. A strong clear blue results, which changes to an opal white if the heating is prolonged unduly. The blue color is due to the formation of tiny crystal nuclei which scatter the light. These particles can be seen under the microscope with 4 mm or higher power objectives, if a horizontal beam of light is projected through a piece of glass on which the microscope is focused. With careful focusing and some adjustment of the illuminating beam, the blue color seen in the field may be resolved into a dense mass of tiny points of blue light. By a suitable length of heating, the partially devitrified Jena glass tubes can be made to give blues ranging from deep indigo to pale sky blue or even to white. The color may be brought out most strikingly by painting the inside of the tube black, so as to cut off all transmitted light. The blues of such specimens are quite wonderful.

The opal glass which is obtained by longer heating undoubtedly contains coarser crystals. Since the color by transmitted light is orange-red, the reflected light must theoretically be a bluish-white; but, actually, the blue is masked by the white. The ordinary opal glass is also theoretically bluish by reflected because it is reddish by transmitted light.[3] Some of the early American candle sticks and door-knobs show a Tyndall blue and so do some of the modern "oven-glasses," not Pyrex. The production of a white color on prolonged heating is a well-known phenomenon.[4] "When glass—especially crown and bottle glass—is exposed to slow cooling during solidification from

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[1] Some of the experiments on which this paper is based were supported by a grant to Messrs. Bancroft, Chamot and Merritt from the Heckscher Foundation for the advancement of Research, established by August Heckscher at Cornell University.

[2] J. Phys. Chem. 27, 222 (1923)

[3] Smull: J. Soc. Ind. Chem. 34, 402 (1925)

[4] Percy: Metallurgy, 25 (1861)

a state of fusion, or if, after it has become cold and solid, it is reheated and kept for a long time at a high temperature, but below its fusing-point, it passes from the vitreous to the crystalline state, when it is said to be devitrified. The so-called porcelain of Réaumur is only devitrified glass. Common barley-sugar, which is sugar in a glassy state, the result of rapid cooling, always becomes devitrified or crystalline on keeping, even at the ordinary temperature. Very beautiful and instructive illustrations of the crystallization of glass may be frequently obtained in glass-houses where either bottle or crown-glass is made; flint-glass, which is composed of silica, potash, and protoxide of lead, rarely occurs crystallized. In pieces of crown-glass the formation of crystals may be traced; little groups of radiating prisms at first appear, which gradually increase in number and size until they finally coalesce into a white opaque mass. In bottle-glass the spheroidal masses are sometimes formed in parallel layers, closely resembling Lipari obsidian. Sections of devitrified glass are beautiful objects under the microscope, when seen by polarized light."

Combustion tubes which have been used a long time often develop quite a marked blue color and I have one specimen of a new piece of tubing, which is quite blue. It probably cooled very slowly for some reason because it certainly was not reheated. Similar phenomena seem to occur in some slags.[1] "The cause of the beautiful colour, which is not infrequently seen in slags from iron-smelting furnaces, has excited much attention. It was ascribed to an oxide of titanium by Kersten, who also referred to the same oxide the blue coloration of the Silesian zinc-retorts, which is very similar to that of the slags in question. He found this oxide in the substance of which the retorts were made. He passed the vapour of zinc over titanic acid heated to redness, and the acid became blue. He then prepared mixtures of the ingredients of which slags are composed, and melted them; but the blue colour was not developed. When, however, they were kept melted at a strong heat in covered crucibles, with the addition of a little titanic acid and zinc, tin, or iron, they became blue. The specimens thus produced were inspected by Berzelius, who regarded the proof as conclusive. Fournet opposed the explanation of Kersten on the ground that certain slags, which were remarkable for the amount of titanium which they contained, were not blue, but grey in the interior and pale yellow on the surface; and that other slags in which there was no reason to suspect the presence of titanium, were blue. He observed, moreover, that when common green bottle-glass is kept heated during a sufficient length of time at a temperature considerably below its melting point, it was rendered opaque and acquired a blue colour similar to that of the slags. I had previously obtained the same result by experiment. Fournet had thin sections made of the glass so coloured, and found that when seen by transmitted light it had a greenish-yellow tint. D'Artigues had before ascertained the same fact. Fournet showed that the powder of the blue slags and blue glass had only a dirty green tint. By melting a silicate of iron and alumina Berthier obtained

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[1] Percy: Metallurgy, 27 (1861)

a glass which, by reflexion, presented a green, almost black tint, but which appeared resin-yellow by transmitted light. From these considerations Berthier inferred that the blue coloration both in the slags and bottle-glass was entirely due to the same cause, namely, the same change in molecular arrangement which occasioned opacity in the bottle-glass. Bontemps, who had had great experience in the manufacture of glass and especially in its coloration, attributes the greenish colour of bottle-glass to oxide of iron combined with carbonaceous matters contained in the mixture. When the temperature is not very high, as, for example, in the covered pots in which flint-glass is made, oxide of iron gives a green colour, more nearly approaching yellow than blue; but when the temperature is high, as in the manufacture of window-glass, the addition of a small proportion of oxide of iron to the mixture produces a glass of a bluish colour. He also remarks that it is known to the manufacturers of bottle-glass, that when the glass is cooled in the pot it becomes opaque blue before being devitrified. He concludes from actual observation that glass may acquire all of the colours of the spectrum from oxide of iron alone; and that these colours are produced in their natural order as the temperature increases. Thus the manufacturers of china and earthenware obtain a purplish-red from sesquioxide of iron at a certain temperature; and at a higher temperature the same oxide yields an orange colour. These temperatures are low as compared with that at which glass is melted; and as has been stated above, the oxide renders glass green at one temperature and blue at a higher temperature. The blue colour of slags has also been referred to vanadium and artificial ultramarine. In respect to vanadium, it may be true that certain blue slags contain this metal, but no satisfactory proof has been advanced that it is the cause of their blue colour; and, in respect to ultramarine, I may state that in numerous experiments I have always found that the colour of ultramarine is destroyed at a temperature much below the fusing point of the compound of silicate and soda, which is termed ultramarine base. On a review of the evidence I am inclined to the belief that oxide of iron is the essential element of the blue colour of the slags."

One may admit the possibility of getting all kinds of colors in glass by means of iron without postulating that all blues are due to iron oxide. The glass which was blue by reflected light and greenish yellow by transmitted light cannot have owed its color entirely to pigment. The opaque blue before visible devitrification sounds like a structural color. The blue color might be due to titanium and yet be a structural color. Robertson,[1] a student under F. P. Dunnington at the University of Virginia, reports that a certain quartz, found in Nelson county, always "presents a characteristic waxy lustre, and a colour varying from pale to deep blue. It therefore appears of interest to ascertain to what this colour is due . . A thin section of the rock was examined under the microscope and found to show throughout the mass a network of extremely thin acicular brown crystals, thus presenting when magnified about 400 diameters an appearance very similar to that of sagenite to the naked eye.

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[1] Chem. News, 50, 207 (1884)

Some of the crystals were twinned, forming the geniculations common with rutile . . . This thin section is decidedly yellow by transmitted light, also shows the threads of iron above referred to, and by reflected light is blue. In view of the blue colour of some varieties of titanic oxide when seen by reflected light, it appears possible that the partial reflection of light by the surfaces of these microscopic crystals occasions the colour in question, or the latter may be in a measure due to the interference of light occasioned by these crystals.

Robertson may have known that he was dealing with a structural color; but he does not make the matter clear. The later people[1] had more definite ideas on the subject.

"By way of contrast it may be of interest here to summarize briefly the results of the investigations into the cause of blue color in some quartz. The occurrence in quantity of beautiful, deep sky-blue, opalescent quartz in quartzose igneous rocks and at times in metamorphosed sediments derived from them, is known in many localities both in this country and abroad, and has been the subject of investigation in a number. This variety of quartz is by no means uncommon in the Southern Appalachians, and is particularly characteristic of some rock types of the Blue Ridge Mountains and its outliers in Virginia.

"The senior writer has examined microscopically many thin sections of blue quartz from different localities in the southeast Atlantic States, and in every case the substance of the quartz was found to be crowded with hairlike inclusions of rutile, which were frequently arranged with more or less crystallographic regularity. On the other hand, quartz of light color or colorless to dark smoky often shows inclusions of rutile needles, with no indication whatever of blue color.

"The blue color of the quartz was apparent in thin sections as well as in hand specimens. There is no evidence, however, that the included crystals of rutile observed in the quartz are blue in themselves, although Dana records among the varieties of color for rutile bluish and violet shades. Of the well-known laboratory tests for titanium, two impart a violet color (1) to the salt of phosphorous bead in the reducing flame when cold and (2) to a hydrochloric acid solution when boiled with metallic tin; but neither compound of titanium (Ti_2O_3 and $TiCl_3$), supposed to produce the color, is known to occur in nature . . .

"Blue quartz occurs as a constituent of the quartz members of the charnockite rock series of India. On microscopic examination Holland found the blue quartz to be crowded with minute hairlike inclusions, presumably rutile, arranged with crystallographic regularity. Concerning the cause of the blue color of the quartz he says[2]: I conclude that the hairlike inclusions to which probably the blue color of the quartz is due, are arranged with crystallographic regularity.

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[1] Watson and Beard: Proc. Nat. Museum, 53, 561 (1917)

[2] Memoirs Geol. Surv. India, 28, II 138 (1900)

"In his studies of the quartz-feldspar porphyry in which are developed phenocrysts of sky-blue opalescent quartz from Llano County, Texas, Iddings,[1] states that the blue color of the quartz "is absolutely due to the reflections of blue light-waves from the minute colorless prisms, whose width is a fraction of the length of light waves. It is similar to the blue color of the sky. It is probable, however, that there is also blue light produced by interference of the light reflected from both sides of the minute tabular crystals whose width is also of the order of a fraction of a light-wave length; so that both kinds of phenomena occur within these quartzes."

"In the comagmatic area of titanium-bearing rocks of Amherst and Nelson Counties, Virginia, deep blue, opalescent quartz both in minute grains and in large masses is an abundant constituent. The blue color of the quartz is pronounced even in thin section, and pressure effects are exhibited chiefly in granulation, fractures, and wavy extinction. The most pronounced microscopic character of the quartz is the presence of abundant, closely crowded, minute, hair-like inclusions of rutile, which are distributed rather unevenly through each grain. After a detailed study of the quartz from this area by Watson and Taber,[2] the following conclusion as to color was stated: "It seems probable that the blue color of the quartz characterizing the rocks of the Amherst-Nelson Counties area is to be attributed to the multitude of hair-like inclusions as explained by Robertson, Iddings, and Holland."

"A different cause of the color of the constantly present blue quartz in the Milford granite of Massachusetts and Rhode Island has been suggested by Emerson and Perry[3] who state that 'a state of strain has probably produced the blue color.' They say, "Most of this quartz is blue, and this color appears also in the contact zones and even in the secondary quartz that is found in fragments of schist which are inclosed in the granite and which have been greatly altered by it. The fractured grains of quartz show with polarized light the strongest undulatory extinction, which indicates that a state of strain has probably produced the color." The authors do not mention at this place (p. 46) the occurrence in the quartz of rutile inclusions, but that they do occur is shown in a previous statement, where the contact effect of the Milford granite on schists is described. They say that these grains are often full of rutile needles, like true granite quartz.

"The blue quartz of the Virginia rutile area is generally characterized microscopically by fractures and microscopically in thin sections of undulatory extinction, but the senior writer attributes the blue color of the mineral to the behavior of light on the minute rutile inclusions and not to any state of strain. This view is strengthened by the fact that heating does not destroy the blue color of the quartz."

Mr. Milligan of the Norton Company, has called my attention to the fact that some of the dark grains of commercial Alundum become bluish by reflected light when roasted. An examination under the microscope shows

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[1] J. Geology, 12, 227 (1904)

[2] Bull. Virginia Geol. Survey, 3A, 214 (1913)

[3] Bull. U. S. Geol. Survey, 311, 46 (1907)

that the grains are not blue by transmitted light and that the apparent color by reflected light is due to the scattering of light by minute inclusions of slag. Mr. Mason has found that the scattered light is polarized and vibrates in a plane perpendicular to the illuminating beam. The polarization effects are complicated by the anisotropic character of the fused-alumina grains. This alters the plane of vibration of the scattered light, just as it might effect light coming from the lower nicol.

Mr. Mason says that "a very interesting property of this Alundum is the apparent variation of its absorption from light to dark brown. The orientation of the 'absorption axis' and the behavior of various sections show striking resemblance to the phenomena of pleochroism; but more detailed examination indicates that the variation in absorption is due to variation in the scattering of light with the change in the index of refraction of the mineral when the plane of vibration of the transmitted, polarized light is changed. For vibrations in one plane the index of the Alundum is much nearer that of the inclusions than for vibrations in a plane perpendicular to this, thus altering their scattering power. The brown, rather than yellow, shade is due to the relative coarseness of the inclusions.

"The above is a general property of anistropic media, in which fine particles are suspended, though apparently it has not been definitely related to the Tyndall blue. Von Fedorow[1] observed it in finely lamellar, birefringent minerals, where it is simply an increased and multiplied example of the effect known as 'twinkling.' Schroeder van der Kolk[2] has ascribed the phenomena to parallel arrangement of the inclusions in the surrounding mineral, which implies that he did not recognize the behavior as related to the Tyndall blue. His assumption is not necessary to account for the behavior."

I have seen Venetian liqueur glasses which were amber-colored by transmitted light and bluish by reflected light. The original glass was probably colored; but the blue was evidently a Tyndall blue and the glasses had either been reheated to produce partial devitrification or had been cooled very slowly. These blues are not especially interesting because the crystals are evidently not small enough and because there is no dark background. A more interesting case is that of the early Chinese porcelain after we have eliminated the contradictions in the various accounts.

Blacker[3] says that "though we read of porcelain blue as the sky, shining as the looking-glass, thin as paper, giving a sound like a musical stone, we could scarcely hope to find a specimen after the lapse of so many hundred years. Besides, if we did, the piece would be unique and even the experts would doubt its identity. Still, the tiny fragments of this precious ware are recognized in China, and are so valuable that the Chinese have them mounted as personal ornaments." From this one would judge that fragments were known and that one could tell from them what color they were. On p. 160 Blacker makes quite a different statement without any cross-reference.

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[1] Pseudo-absorption, Z. Kryst. 22, 128 (1900)

[2] Sammlung Geol. Reichsmuseum Leiden, 6, 89 (1900)

[3] Chats on Oriental China, 93 (1918)

"We read that in 954 A. D. the Emperor Chin-Tsung ordered some vases to be made which should be as blue as the sky after rain when seen between the clouds, and it is said that his celebrated porcelain was of this blue, fine like a looking-glass, thin as paper, and giving a sound like a musical stone, the only defect being that the feet of the pieces were of a coarse yellow clay. Alas for the romantic story! The most recent catalogue of the Musée Guimet at Paris, drawn up by the national experts with the assistance of such Chinese experts as were available, states that the story is all a mistake. The word which was translated 'blue' should have been translated 'green' which brings us back again to Céladon."

Burton[1] puts more definitely what Blacker was probably trying to say "The Ju-yao was the ware made at Ju-chou in the province of Honan. This was supposed to be a reproduction of one of the earlier mythical wares which was described as blue as the sky after rain when seen between clouds. Dr. Bushell mentions a fine piece of Ju-yao in his possession, which, however, has a delicate greenish glaze with no trace of blue. This is one of those pieces with a refractory glaze of such sluggish fluidity that it has never flowed over the whole piece. There seems little doubt that this ware was an early type of Céladon, and we shall probably be nearer the Chinese meaning if we read green as the sky after rain, etc."

What Burton[2] has to say about the porcelain of the Sung period is also very interesting. "When we ask for authentic specimens, all the authorities are agreed that no porcelain pieces are now known which are earlier than the Sung dynasty (960-1259 A. D.), while the Sung productions have become so scarce that they are hardly to be procured by the most princely purse, even in China itself. We may read poetic accounts, by ancient Chinese writers, of early porcelains made before the times of the Sung emperors as being sky-blue in colour, brillantly glazed, thin as paper, and emitting a clear musical note when sounded; but nothing even remotely approaching such a wonderful description has survived to our time . . . It may be pointed out that there is not a word in this description which would distinguish porcelain from any other species of hard-fired pottery, and that, indeed the characteristic quality of translucence is never mentioned in any of the ancient accounts of the so-called porcelains. Perhaps a potter may be allowed to add that a careful examination of the best authenticated specimens of the wares attributed to the days of the Sung dynasty leaves little doubt that we are here in the presence of the very birth of Chinese porcelain, when the first steps were being taken which ultimately led to the appearance of the perfect ware. If we examine all the specimens in the best European collections that can with any probability be ascribed to the Sung epoch we find only heavy, even clumsy, pieces of moderate size and great solidity, with a thick dullish glaze on a dense opaque body, so that it is difficult to decide whether the ware should be regarded as porcelain or as stone ware . . .

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[1] Porcelain, 57 (1906)

[2] Porcelain, 53 (1906)

"The ancient glazes and bodies were made from minerals far less carefully washed and prepared than those we have spoken of in the previous chapters. The dark colour of the body is one proof of this—the imperfect nature of the glazes furnishes additional proof. Yet from these defective materials the early Chinese potters managed to win many artistic triumphs; for the glazes from their very want of clearness and homogeneity of structure, are famous for their opalescent quality. This opalescence manifests itself in a variety of ways; sometimes the glaze is delicately veined with lines of more opaque whiteness; sometimes it is irregularly splashed or blotched with soft cloudings, which render the glaze-colour so subtle and delicate that it reminds one of the changing lights on the breast of a dove, or the play of translucent shadows in a piece of Mexican onyx. At times the opalescent cloudings or veinings in the glaze appear of a delicate brilliant blue—no doubt from the way in which the light is scattered by these infinitely fine, white particles.[1] This blueness has generally been attributed to the use of cobalt in the glaze, but I am strongly of the opinion that cobalt was so seldom used that we may leave it out of account among the genuine Sung pieces. It is impossible to describe, except to those who had the privilege of handling and examining actual specimens of these wares, how much the artistic charm of these forerunners of true porcelain is dependent on the vaporous softness imparted to the glaze by this opalescent quality, nor how much the later porcelain makers sacrificed, in certain directions, in their attempts to obtain that pure and uniformly white glaze so necessary for the display of painted decoration.

Holson[2] writes that "it is equally certain that many of the changing tints in the thick, uneven, bubbly glazes of the Sung vases are due to opalescence alone. This has been proved to demonstration by Mr. Burton, who has produced from his kilns a porcelain glaze with passages of pale lavender, and even flushes of warm red, by using nothing but a thick opalescent glaze entirely innocent of colouring matter." From this statement one would not gather that the glaze was sky blue; but Professor J. N. Collie assures me that it is and that, while there is a trace of iron in it, the color cannot be due to iron.

Professor Collie was good enough to give me two small fragments of a Sung blue glaze. The first has a fine, deep sky-blue color by reflected light and is yellowish by transmitted light. The second was originally like the first; but had been fused by Professor Collie and is no longer blue. Mr. Mason examined the blue sample for polarization and reports that the blue is unquestionably a Tyndall blue. While this would show up fairly well against the gray or drab body of the Sung porcelain, it would be very much more effective on a black base and one would like very much to see a vase with a really fine blue on a black background. There would be no difficulty nowadays in making a much better blue than the Chinese did because we understand the conditions

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[1] We may note that the blue and purple streaks or patches so often seen in the finest Flambé pieces produced in the eighteenth century are due to the same cause, though they, too, have generally been erroneously attributed to the presence of oxide of cobalt.

[2] Chinese Pottery and Porcelain, 50.

for maximum effectiveness. It is interesting to note however that the Chinese were using Tyndall blue for decorative purposes nearly a thousand years ago.

Orton[1] reports that a glass mixture of equimolecular parts of sodium oxide, calcium oxide, and silica gave "a rough, coarsely vesicular silicate, composed of various colors—gray and bright sky-blue predominating. It appears wholly stony at first sight, but, on close examination, is seen to be a mass of crystalline matter, some of the crystals being clearly distinguished by the unaided eye. It was apparently not well fused, and was the only one of the series giving evidence of too little fusion. The colors are distributed irregularly, and the blue is a prominent factor in it. What this mineral is, cannot be even guessed, but it seems evident that the amount of silica present is too small to actively engage all of the Na_2O and the CaO, and hence several compounds, of quite diverse character, have been formed and are mingled in the slag."

While the experimental data, as given, are quite insufficient to prove that Orton was dealing with a Tyndall blue, this is a more plausible guess than to assume the existence of an unknown, and purely hypothetical, blue mineral. These experiments should be repeated.

There are one or two other things which should be cleared up at the same time.[2] "Solutions of baryta, when kept in glass bottles for any length of time, deposit transparent rhombic crystals of the composition $BaSiO_3 \cdot 7H_2O$. These crystals lose their water a little above 100°, and become turquoise-blue."

Viola[3] has studied the blue shimmer of the moonstone and finds that it is a Tyndall blue. He is not quite certain what the particles are which constitute the turbid medium. In the case of albite it seems to be crystals of albite itself. If the Ceylon moonstone, which he was studying, is cut into thin plates more than one millimeter in thickness, these are milk-white. With a thickness of one millimeter, the plates are practically transparent. The scattered blue light increases in intensity as the thickness of the plate decreases, reaching a maximum when the thickness is 50μ.

It has been known for many years that there is no blue pigment in any feather. Over twenty years ago Haecker and Meyer[4] showed that the blue was a Tyndall blue, the light being scattered by myriads of minute pores in the horny mass of the feather, and the blue being made visible by a background of dark pigment which prevented the transmitted light from reaching the eye. Similar conclusions were reached by Mandoul[5] whose work seems to have been overlooked completely. The identification of the blue of feathers as a Tyndall blue has been accepted by some of the physicists,[6] but not by the zoologists. Just recently, Haecker's work has been confirmed and extended by Mason[7] at Cornell and there can no longer be any question of the accuracy of Haecker's views, especially since Mason has succeeded in making the struc-

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[1] Trans. Am. Ceramic Soc. 5, 312 (1903)
[2] Thorpe: Dictionary of Applied Chemistry, 1, 549, 564 (1921)
[3] Z. Kryst., 34, 171 (1901)
[4] Zool. Jahrbüch, Abt. Syst. Geog. Biol. Tiere, 15, 267 (1901)
[5] Ann. Sci. Nat., Zool. 18, 225 (1903)
[6] Chwolson: Traité de Physique, 2, 354 (1906)
[7] J. Phys. Chem. 27, 201 (1923)

tural blue tubes referred to in the beginning of this paper, and in duplicating the appearance and behavior of blue feathers with a Tyndall blue, collodion jelly, which is porous. The blues made synthetically by Mason in glass are quite as gorgeous as any of the Tyndall blues to be found in feathers. It is probably because Haecker did not make a good structural blue that his views were not received with much favor. He has, however, come into his own now.

Since some light can be scattered by dust-free gases and liquids, Strutt[1] has made "an examination of the behaviour of solids in this respect. At the first trial it was found that glass scatters very freely, the scattered light being blue, and in many cases almost completely polarised . . . Numerous specimens of plate glass and optical glass have been examined. These all show the scattering, though they differ among themselves in respect of intensity and completeness of polarisation. The depth and purity of the blue colour goes of course with the latter . . .

"These glasses give a polarisation of the same order as the various gases where the scattering is molecular. This however is probably an accidental circumstance. In the case of glasses, the wide difference between different samples suggests that scattering is due in the main to inclusions rather than to the molecules. These inclusions are probably to be regarded as spherical, some of them with a diameter not small compared with the wave-length. In this case the defect of polarisation in glass would be due to the appreciable size of the obstacles, whereas in gases it is due to lack of symmetry.

"The remaining experiments on solids have reference to quartz in different varieties and to Iceland spar. It was found that yellow quartz and smoky quartz have the property of scattering light very strongly, the colouring matter being evidently distributed in the crystal in the form of small particles analogous to those found in glass. Preliminary examination of a crystal can often be made by immersing it in a trough of highly refracting material such as benzene; but to work satisfactorily, it is necessary to have suitable faces cut and polished, so that the beam can be sent along the axis of the crystal and examined perpendicularly to it. Evidently the scattered light should be analysed parallel and perpendicular to one of the principal planes of the crystal, for if this is not done, double refraction altogether disturbs the relative intensities of the images.

"With a crystal of yellow quartz from Madagascar, the polarisation of the scattered light was tolerably complete, the weak image having about 0.7 per cent of the intensity of the strong one. This is decidedly more perfect polarisation than was obtained with any of the gases examined in the earlier investigation. The stronger image was bluish, but the fainter image was a very rich blue, no doubt the same as the 'residual blue' observed by Tyndall in precipitated clouds, when the particles were no longer very small compared with the wave-length. A sample of smoky quartz from Brazil gave less intense scattering than the above; the scattered light was, however, of a good sky-blue colour. The weak image had about three per cent of the intensity of the strong one . . .

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[1] Proc. Roy. Soc. 95 A, 476 (1919)

"Intensity comparisons were made between the total light scattered by clear quartz and by the other media, by the method formerly described, of altering the lens aperture until photographic intensity was equalised. The results were as follows: dust-free air, 1; clear quartz, 8; plate glass, 300; liquid ether, 900. This last is the old result for liquid ether and represents the least scattering I could get, after treating the ether in various ways. I am not satisfied that it is a really definite result for pure ether. The problem of obtaining such a result is far more difficult for liquids than for gases. I have also observed a scattering, strong compared with that of air, in a rhomb of clear Iceland spar. No intensity measurements were made.

"It is probable that even in the clearest crystals, the residual scattering is of the same character as that seen in obviously smoky quartz, and is due to inclusions which have no relation to the crystalline structure. Different specimens of apparently clear quartz vary considerably in their scattering power a fact which can hardly be explained on any other view. The numbers above quoted for quartz and glass are merely illustrative, and refer only to the particular specimens.

"The molecules in the crystal are regularly spaced, and at a distance apart small compared with the wave-length of light. So far as they are concerned, the crystal behaves like a diffraction grating with its spacing less than the wave-length. Under these circumstances the secondary disturbances destroy one another by interference, and there is no molecular or atomic scattering. With much shorter waves (X-rays) the well-known diffraction by crystals comes into evidence."

The Tyndall blue that we get with light-colored powders on a dark ground is not really a case of Tyndall blue in solids because the external phase is air; but it seems worth while to include it.

Koyl[1] says that "those who are familiar with the methods of blow-pipe analysis have observed faint borders occasionally surrounding some of the colored charcoal coatings, the colors of these borders seemingly bearing no relation to the characteristic colors of the adjoining oxides. For instance, the white coating of antimony is generally accompanied with a blue border, the brownish oxide of cadmium occasionally with a green, while the lead and bismuth yellows not unfrequently have a whitish ring inclosing them. As these occur only and always where the coating is very thin they have a significance different from that of the ordinary colors, and as they may be produced at pleasure from the purest specimens they cannot be due to mixtures of the metals. A possible analogy with the antimony blue was suggested by a consideration of the colors of the sky, and to prove the connection it was simply necessary to show the similarity of attendant phenomena. As is well known, it is believed that the blue of the sky is due to the presence in the atmosphere of suspended particles, so fine that they are unable to reflect the longer rays of the spectrum which accordingly are transmitted and the union of the remainder gives to the sky its blueness. At evening, the sky is red

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[1] Am. J. Sci. (3) **20**, 187 (1880)

because we get the rays of the sun directly transmitted or reflected from the clouds. Thirdly, the light of the sky, reflected at an angle of 90° with the sun, is plane polarized.

"When an antimony coating had been produced which gave, beyond the white oxide, a blue well-defined and full, the whole was illuminated in a dark room by a sodium flame and that the blueness was no psychical or physiological effect as distinguished from ordinary vision was proved by the fact that here it almost completely vanished while the white presented the usual ghastly appearance. A blue book-cover, treated in the same manner, gave more reflection than did the blue coating.

"Experiments with the polariscope were at first inconclusive from the fact that though the light from the blue coating was largely polarized, so, to some extent, was also that irregularly reflected from the charcoal, and it was found necessary to cover the block with a thin layer of carbon from a gas-flame. The repetition of the test then showed that the proportion of light polarized by the layer of carbon, at the given angle, was almost nothing; that by the thick white coating, small; while on the blue the phenomenon was almost complete. What light here was not polarized was evidently reflected from the larger particles mixed with the fine, for the analyzer, while it did not totally extinguish the light, yet excluded nearly all appearance of blueness.

"In order to determine the character of the transmitted light, a microscope covering-glass was inlaid in the charcoal and the oxidation so executed that the glass was in the center of a small area all of which was blue. On removing the glass, the light which passed through, proved to be of the expected yellow, though less brilliant than anticipated. The color might be seen either by transmitting the direct light of the sun or by placing the glass at such an angle that total reflection was produced and thus in the passage of the rays through the layer to the glass and out through the layer to the eye the blue was principally lost and only the mixture of longer rays appeared. Viewed through a microscope, the result was the same. I have since, however, improved upon this plan by the more convenient method of covering with carbon a piece of ordinary window-glass, three inches by two, and then projecting the oxide upon the opposite surface of the plate. There is thus no difficulty in distinguishing a very slight amount of color in the coating and for transmitted light, any portion of the carbon may be easily removed.

"This case, a type of all charcoal coatings which shade off to blue in thin layers, appears thus parallel to that of the sky color and the theory which is accepted for the one will also satisfactorily explain the other.

"To account for the cadmium green we have only to note that if the substance upon which we are experimenting has the power of absorbing the shorter rays of the spectrum, the reflected light would from a heavy coating be yellowish or reddish, the particular shade depending upon the amount of absorption of violet and blue; and the formation of a layer as thin and of particles as fine as before should result in giving us the color of the shortest rays which the substance is capable of reflecting, viz: in this case, green. The coating of cadmium has exactly this appearance and shows the effect of the gradual transmission of red by shading from the original color (dark red) through yellow into a fine green. As before, the light reflected from the thin layers is highly polarized and the rays which pass through form a deep, dark red. In exceptional cases, it is possible to produce such a thin coating that the extreme edge is fringed with a faint blue.

"The other case, lead, is now easily explained. This metal gives a coating of which the color is a beautiful chrome yellow, and regarding this merely as a repetition of the preceding phenomenon and the yellow as compounded of rays from the whole range of the spectrum but not in the upper proportion to form white, the line of thought suggested evidently is that if the layer be decreased in thickness regularly from the center to the circumference of the charcoal, there ought to be, at some distance from the centre, a zone within which sufficient red should be transmitted to equalize the amount of blue lost by absorption and the reflected rays should form a yellowish white. Beyond this, as the thickness of layer still decreased, the color should be blue for the same reason as in the cases of antimony. The white zone is easily produced and the blue border, which always surrounds it, polarizes the light as before and transmits orange colored rays.

"The theory, once given, serves to explain nearly all the anomalous colorings of the charcoal coatings:—the bluish borders which occasionally skirt almost any of the metallic oxides, the "peacock tails" of cadmium, etc., and thus does away with the necessity of supposing the presence of impurities (though, by the way, no impurity would solve the problem in the case of the cadmium green.)

"From a physical standpoint, the experiments seem interesting as an extension of our knowledge of the action of these small particles upon light. Had not the subject presented itself in this way, we would scarcely have guessed that such a change in reflecting power could have been produced by so small a change in size and thickness."

Merwin[1] has made quite a study of the behavior of white pigments, both alone and mixed with black. "The most important characteristics contributing to the efficiency of a white pigment are non-absorbing power, high refractive index, weak optical dispersion, fineness and evenness of grain. If optical dispersion is strong, the reflecting power for blue and violet light may be so much greater than for red as to give the pigment a bluish color under certain conditions. There is a critical size of grain for each homogeneous white pigment, depending upon the optical properties of the grains and vehicle and the distribution of the pigment grains. This size is from about 0.5 to 1.0μ. Larger grains have too little reflecting surface per volume of substance, and grains much smaller do not act as regular reflectors at all unless very close together, but they scatter light. Grains having a diameter close to a wavelength of green light in oil—0.35μ—may reflect violet more strongly than red. Neither scattering, nor the differential reflection just referred to, have

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[1] Proc. Am. Soc. Testing Materials, 17 II, 503 (1917)

significant effect on the tint of a white pigment, provided the grains are close together and in a thick film, as they are on a well-painted surface. For, although the red penetrates deeper, it is finally scattered or reflected to practically the same degree as the blue. But if the film is thin or the particles are widely spaced, considerably more red than blue finds its way through the film. Suppose such a film covers a black surface, then the excess of red is absorbed by the surface and the film-covered surface has a blue-gray appearance.[1] A white pigment containing no grains less than 2μ in diameter under the same conditions produces a neutral gray. In certain mixed pigments these effects of size of grain are very pronounced.

"Samples of the various white pigments were tested over a black surface. All of them gave more or less bluish grays, dependent upon the amount of very fine grains which they contained. Search was then made amongst a large assortment of chemicals— in the form of white powders—to find one which would produce over black a true neutral gray, and which would also be a fairly 'strong' white. A sample of lead sulfate was found satisfactory. Its grains ranged between 2 to 5μ. This sample may be called a 'true' white."

"Most of the zinc-oxide pastes contain enough material finer than 1μ to add considerable blue color, due to scattering somewhat, to paints in which they are mixed, and to reduce the hiding power of the paints . . .

"The true white previously described was mixed with several black pigments to produce grays. Graphite and lampblack produced neutral grays, but ivory black and magnetic oxide black produced slightly brownish (orange) grays. The finest grain French-process zinc oxides, with graphite and lampblack, produced very blue grays; some contained as much as 10 per cent blue. American-process zinc oxides and other commercial white pigments gave grays containing 2 to 5 per cent blue. Thus, in mixture with black, these fine-grain whites give blue grays which are, however, less blue than may be produced over a background of black. The orange tinge of grains of ivory black and magnetic-oxide black may neutralize the blue which white pigments produce in mixtures, so that neutral grays can be made. A test was made to determine how much blue would be required to be mixed with a true white, to give ivory black a blue-gray like that produced by graphite and White-Seal zinc oxide. The blue pigments used were ultramarine, Prussian blue, and true cobalt blue. It was found that a bright blue, corresponding to 70 to 80 percent blue, was required." Mr. Clyde Mason has called my attention to the fact that the bluish bloom on some fruits and the blue color of the blue spruce are Tyndall blues, the light being scattered by fine hairs or fine powder. The intermediate blue stage before varnish has been made white by water is a Tyndall blue, though the details have not been worked out. This article shows that Tyndall blues in solids are not infrequent in nature and in art. This account is not exhaustive and it is hoped that more cases will be described now that attention has been drawn to some of the types.

Cornell University

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[1] A blue of considerable brilliancy (blue 25 parts, neutral gray 75 parts) can be produced by pressing a film of very fine-grain zinc oxide paste very thin, under a cover glass on a glass slip blackened on the under side.

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THE FORMATION OF ARSENATE JELLIES

BY HARRY B. WEISER AND ALLEN P. BLOXSOM

Historical

Forty years ago Grimaux[1] made the interesting observation that the dialysis of a colloidal solution of ferric arsenate peptized by ferric chloride resulted in the formation of a firm transparent jelly having a reddish yellow color. More recently Holmes and his pupils[2] have extended the investigations of Grimaux and have found that firm jellies are obtained by the dialysis of colloidal solutions of ferric arsenate peptized by NH_4OH, HCl, HNO_3 $FeCl_3$, and $Fe(NO_3)_3$ but not by H_2SO_4 or $Fe_2(SO_4)_3$. Similarly jellies were obtained by dialysis of a solution of cadmium arsenate peptized by $FeCl_3$ and of solutions of arsenates of chromium and aluminium peptized by their respective chlorides. Ferric arsenate was prepared by adding ferric chloride to an excess of alkali arsenate. The latter is absorbed strongly but a great deal can be removed by washing. The unwashed precipitate peptized by $FeCl_3$ sets to a jelly more quickly than if the precipitate is washed. The precipitate obtained with different arsenates of the alkali metals required different times to set. Those prepared with the ammonium salt set most quickly and with the lithium salt least quickly, the accelerating influence of the series decreasing in the order $NH_4 > K > Na > Li$.

In a later communication Holmes and Fall[3] pointed out that the formation of a jelly by dialysis of a colloidal solution of ferric arsenate peptized by $FeCl_3$ was probably due to the slow removal of the acid derived from hydrolysis of ferric chloride. It was thought that the equilibrium represented by the following equation was set up:

$$Fe_2(HAsO_4)_3+6\,HCl \rightleftarrows 2\,FeCl_3+3\,H_3AsO_4$$

and that dialysis removed HCl permitting the separation of ferric arsenate in the form of a jelly. It seemed probable that the same result could be obtained by decreasing the hydrogen ion concentration by the addition of a base; but when this was attempted a lumpy precipitate and not a jelly was obtained. However jellies were prepared by allowing NH_4OH, $Ca(OH)_2$, or $NaC_2H_3O_2$ to diffuse slowly into the colloidal solution through a membrane of goldbeater's skin.

Coloriano[4] obtained a rose colored jelly by adding a solution of arsenic acid to a warm solution of manganese carbonate. The jelly broke down

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[1] Compt. rend., 98, 1540 (1884)

[2] Holmes and Rindfusz: J. Am. Chem. Soc., 38, 1970 (1916); Holmes and Arnold: Ibid 40, 1014 (1918)

[3] J. Am. Chem. Soc., 41, 763 (1919)

[4] Bull. 45, 711 (1886)

quickly with the formation of crystals having the composition $MnHAsO_4 . H_2O$. Diesz[1] prepared a clear stable jelly by mixing solutions of $MnCl_2$ and KH_2AsO_4. The primary arsenate $Mn(H_2AsO_4)_2$ is very soluble[2] and the jelly was found to consist of $MnHAsO_4$ formed in accordance with the following reaction:

$$Mn^{\cdot\cdot}+H_2AsO_4{}'=MnHAsO_4+H^{\cdot}$$

Since an equilibrium is set up, the quantitative precipitation of the manganese as $MnHAsO_4$ is impossible but the amount thrown down may be increased by adding an excess of KH_2AsO_4 or by heating. If the hydrogen ion is neutralized by ammonia so as to displace the equilibrium to the right some $AsO_4{}'''$ ions is formed and a mixture of the secondary and tertiary salts results. Jellies containing tertiary arsenates were found to be cloudy.

Klemp and Gyrlay[3] obtained arsenate jellies by adding ammonium sulphate, acetic acid and an excess of sodium arsenate to solutions of salts of zinc, iron, manganese and cadmium. Later Diesz[4] called the attention of Klemp and Gyrlay to the work on manganese arsenate jellies, after which they found that good jellies of zinc arsenate and cadmium arsenate could be obtained without the use of ammonium sulphate by mixing a solution of the metallic salt either with a solution of Na_3AsO_4 neutralized by some acid or directly with KH_2AsO_5.

Theoretical

Structure. A large amount of work has been done by a number of investigators in an attempt to determine the structure of jellies. Although there is considerable difference in opinion as to the exact structure, it is now quite generally recognized that the formation of a network is an important step in the process of jelly formation. In 1858 Nägeli[6] advanced the theory that jellies owe their characteristic properties to a loose network or aggregation of ultramicroscopic or amicroscopic particles. This view was elaborated by Zsigmondy and Bachmann[7] in 1912 and has been supported by recent investigations on silicic acid jellies by Anderson[8], on starch-water jellies by Meyer[9] and on soap jellies by Bachmann[10] and McBain[11]. As might reasonably be expected the exact nature of the network varies considerably in different cases. In certain cases the structure appears grainy and, in others, definite fibrils or filaments have been observed, particularly in the soap jellies of Bachmann and McBain. The filaments, where these occur, likewise show individual variations. Thus, Flade[12] in 1913 from a study of barium malonate

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[1] Kolloid-Z., **14**, 139 (1914)

[2] Schiefer: Z. gesamt. Naturwiss., **23**, 347 (1864)

[3] Kolloid-Z., **15**, 202 (1914)

[4] Ibid., **16**, 16 (1915)

[5] Ibid., **22**, 57 (1918); **28**, 262 (1921)

[6] Nägeli and Schwendener: Das Mikroscop, 2 Ed. (1877); Theorie der Gärung, (1879)

[7] Zsigmondy: Z. anorg. Chem., **71**, 356 (1911); Kolloid-Z., **11**, 145 (1912); Bachmann: Z. anorg. Chem., **73**, 125, (1912)

[8] Z. phys. Chem., **88**, 191 (1914)

[9] Kolloidchem. Beihefte, **5**, 1 (1913)

[10] Kolloid-Z., **11**, 145 (1912)

[11] Laing and McBain: J. Chem. Soc., **117**, 1506 (1920)

[12] Z. anorg. Chem., **82**, 173 (1913)

jellies concluded that jellies in general consist of a texture of probably crystalline threads; while Stubel[1] in 1914 pointed out the resemblance of jelly filaments to linear crystals; and Howell[2] in 1916 introduced the term crystalline gel. Bradford[3] considers gel formation as a process of crystallization; Moeller[4] likewise believes that threadlike crystals form a lattice that entrains the liquid; and von Weimarn[5] concludes from his investigations that a jelly is a sponge composed of highly disperse, crystalline granules soaked in dispersive medium. The view that gel formation is merely a process of crystallization is contradicted by the investigations of Barrett[6] and McBain[7] although both of the latter are strong supporters of the filamentous structure. Bogue[8] considers gelatin jelly to be made up of streptococcal threads of molecules. Harrison[9] agrees that many jellies possess a fibrilar structure but he obtained photographs of gelatine and cellulose jellies that showed the presence of minute particles joined together in a somewhat irregular manner. Alexander[10] believes that the polar nature of molecules may tend to produce some kind of orientation and that some chain-like structures may be formed; but that the formation of chains or threads is not an essential of gel formation. He admits however that polar groupings in chains probably takes place to a considerable extent in dilute solutions of gelatine. It seems to me altogether unlikely that jellies of widely different substances should be essentially identical in structure; but investigators have apparently sought to establish such an identity. Studies on specific jellies have led some to conclude that all jellies are made up of amorphous threads, others that they are all composed of crystalline threads and still others who fail to find any threads or filaments at all but observe an irregular grouping of particles. Doubtless all are right in specific cases so that it would seem that in order to get a jelly all that is necessary is to precipitate uniformly throughout a solution a very finely divided crystalline or amorphous substance that adsorbs the solvent very strongly. These finely divided particles may form fibrilar threads or they may unite in a more irregular fashion forming trees, radials or something analogous to a string of beads. The resulting network of myriads of hydrous particles constitutes the gel structure. The amount of the dispersed phase that must be present to form a firm jelly is determined by the size of the particles and the extent to which they adsorb the dispersing liquid.

Formation of concentrated jellies: von Weimarn's Theory. Von Weimarn[11] made a systematic study of the form in which substances precipitate from solution. He pointed out that precipitation depends on a number of very

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[1] Pflüger's Archiv, **156**, 361 (1914)
[2] J. Physiology, **45**, 26 (1916)
[3] Biochem. J., **12**, 351 (1918)
[4] Kolloid-Z., **23**, 11 (1918)
[5] J. Russ. Phys. Chem. Soc., **47**, 2163 (1915)
[6] Biochem J., **14**, 189 (1920)
[7] Loc. cit.
[8] Chem. Met. Eng., **23**, 61 (1920); J. Am. Chem. Soc. **44**, 1343 (1922)
[9] "The Physics and Chemistry of Colloids and their Bearing on Industrial Questions", 57 (1921)
[10] "Glue and Gelatine", (1923)
[11] "Grundzüge der Dispersoidchemie", 30, (1911)

different factors; on the solubility of the substance; on the latent heat of precipitation; on the concentration at which the precipitation takes place; on the normal pressure at the surface of the solvent; and on the molecular weights of the solvent and the solute. He points out the impossibility of taking all of these factors into account and simplifies the problem by considering first but two of the factors, the solubility of the precipitating substance and the concentration at which precipitation begins. The effect of viscosity is discussed briefly in a later work[1]. The process of condensation (precipitation) is divided into two parts; the first stage, in which the molecules condense to invisible or ultramicroscopic crystals; and the second, which is concerned with the growth of the particles as a result of diffusion. The velocity at the important first moment of the first stage of the precipitation is formulated thus:

$$W = K\frac{\text{Condensation pressure}}{\text{Condensation resistance}} = K\frac{Q-L}{L} = K\frac{P}{L} = K\,U$$

where W is the initial rate of precipitation; Q the total concentration of the substance that is to precipitate; L the solubility of coarse crystals of the substance; $Q - L = P$, the amount of supersaturation. The ratio $P/L = U$ is the percentage supersaturation at the moment precipitation begins.

The velocity of the second stage is given by the Nernst-Noyes equation:

$$V = \frac{D}{S}.O.(C-l)$$

where D is the diffusion coefficient; S the thickness of the adherent film, O the surface, C the concentration of the surrounding solution and l the solubility of the dispersed phase for the given degree of dispersity. C-l may be termed the absolute supersaturation.

From these general formulations von Weimarn arrives at the conclusion that jellies are obtained only when the ratio P/L, that is, the percentage supersaturation U, can be made enormous. It is pointed out that the nature of a precipitate is quite different depending on whether a given value of U is obtained by a large P or by a small L. If a large U is obtained by a high value of P, a large amount of disperse phase is produced and a gel forms while if P is small and L very small, a relatively small amount of disperse phase is produced and a sol is formed. Von Weimarn has demonstrated the accuracy of his deductions in a large number of cases using reacting solutions of high concentrations; and it is apparently true that any salt can be obtained in a gelatinous form if the concentration of the reacting solutions and so the velocity of precipitation is sufficiently high. Thus von Weimarn[2] prepared jellies of substances like $BaSO_4$ which usually precipitate in the form of crystals by mixing very concentrated (3 N - 7 N) solutions of manganese sulphate and barium

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[1] Zur Lehre von den Zuständen der Materie, 21, (1914); Kolloidchem. Beihefte., 4, 101 (1912)

[2] "Zur Lehre von den Zuständen der Materie", 21 (1914)

thiocyanate. This is not the condition under which jellies are usually obtained, and their existence is temporary. By mixing very high concentrations of materials that react to form an insoluble precipitate, a very large number of particles are formed because of a high degree of supersaturation.[1] Each of the myriads of minute particles adsorbs a little water and so the whole amount of liquid is enclosed thus forming what has been termed a jelly. These so-called jellies break down on standing on account of growth of the particles and the consequent liberation of adsorbed water. I do not believe that precipitates in which the ratio of moles of water to moles of salt is say 20 : 1 or 25 : 1 should be considered as jellies in the same sense as precipitates in which this ratio is two or three hundred times as great. Very finely divided sand or Fuller's earth may be matted in the bottom of a test tube and this solid will take up a great deal of water before a supernatant water layer is observed; but I should not call such a preparation a jelly. It seems to me that von Weimarn's barium sulphate jelly may be similar except that the particles are much smaller and so a given amount will take up more water. On the other hand with true jellies where the amount of enclosed water may be relatively enormous, time must be allowed for the formation of a definite structure. As a matter of fact von Weimarn[2] recognizes a difference between a $BaSO_4$ jelly prepared by his method and a jelly formed by uniform gelatinization of a liquid throughout its mass as in the case of gelatine jelly. The former he terms a "coarsely cellular gel" and the latter a "reticulated gel." Be this as it may, the important thing is that von Weimarn's method is not the usual one for obtaining dilute jellies.

Formation of jellies by precipitation from colloidal solution. Since finely divided particles that adsorb water strongly are of primary importance for the formation of a hydrous jelly it would seem that the most promising method of preparing dilute jellies would be to precipitate hydrous substances from colloidal solution. The von Weimarn theory tells us, of course, that this precipitation would have to take place at a suitable rate under conditions that are not conducive to growth of the individual particles; but it does not enable us to predict the optimum rate of coagulation, the effect of salts on jelly formation or the conditions that determine the formation of a jelly rather than a gelatinous precipitate. As a result of recent investigations on the formation of typical dilute inorganic jellies I have outlined the general conditions of jelly formation and the effect on the process of various factors other than the percentage supersaturation "at the important first moment of the first stage of condensation" from molecules to invisible crystals. Jellies would be expected to form from colloidal solution if a suitable amount is precipitated at a suitable rate without agitation in the absence of a medium that exerts as appreciable solvent or peptizing action. If the concentration of the colloid is too low, no jelly or only a very soft jelly can result. If the velocity of precipitation is too great, contraction is likely to occur with the formation of a gela-

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[1] Bancroft: J. Phys. Chem. 24, 100 (1920)
[2] J. Russ. Phys. Chem. Soc., 47, 2163 (1915)

tinous precipitate instead of a jelly. The effect of the presence of salts on jelly formation is therefore determined in large measure by the precipitating and stabilizing action of the ions in so far as these affect the rate of precipitation. In general a slow rate of precipitation is to be preferrred if there is no tendency of the particles to grow as a result of the solvent action of the electrolyte. The favorable concentration for different electrolytes is in the immediate region of their precipitation concentration. A little below this value no precipitation or only a slight precipitation takes place while above this value coagulation is usually so rapid that a gelatinous precipitate is formed instead of a jelly. The reason is that time is not allowed for uniform mixing of the colloid with coagulant and the slow uniform precipitation that is necessary for the building of a uniform jelly structure is replaced by rapid uneven coagulation and the consequent contraction that distinguishes a gelatinous precipitate from a jelly.

Formation of jellies by dialysis. From the point of view outlined in the foregoing section, the formation of jellies by dialysis of a colloidal hydrous substance is readily understood. Dialysis merely removes the stabilizing ion slowly and uniformly below the critical value necessary for peptization and precipitation results just as if the adsorption of the stabilizing ion were compensated for or neutralized by the addition of an electrolyte having a suitable precipitating ion.

Formation of dilute jellies by metathesis. The von Weimarn theory tells us that mixing dilute solutions that interact at once will not give a jelly since the percentage supersaturation P/L = U is too small because of the small value of P. As a matter of fact however jellies have been obtained under certain conditions by mixing quite dilute solutions in which P is small and in which L is sufficiently large that precipitation is slow and quantitative precipitation impossible so that P/L = U, is quite small. Such cases are apparently not covered by the von Weimarn theory. It is quite possible to obtain a gelatinous precipitate by mixing dilute solutions of two salts which precipitate immediately (P small; but L very small) but a jelly will not form under these conditions. The reason is evident when we consider the impossibility of getting the instantaneous mixing of the solutions which is essential for uniform precipitation throughout the solution. One part is precipitated before another is mixed with the precipitant and the homogeneity which is characteristic of a jelly is lost. Moreover the mixing itself will tend to destroy the jelly structure. The results are therefore not unlike those obtained when a colloid, capable of forming a jelly by slow precipitation, is coagulated too rapidly by the addition of excess electrolyte. To obtain a jelly from a colloidal solution it is necessary to add such an amount of electrolyte that thorough mixing is possible before appreciable coagulation takes place. From these considerations it follows that precipitation of a hydrous substance as a result of double decomposition might form a jelly instead of a gelatinous precipitate in case the thorough mixing of the solutions could be effected before precipitation begun and in case the precipitation once started proceeded at a suitable rate. Such conditions do not obtain as a rule; but they are quite possible theoretically. Thus the precipitation may be the result of a step-wise reaction, one step of which proceeds at a suitably slow rate. It is further possible to have a reaction that proceeds very slowly at low temperatures but with marked velocity at higher temperatures. This would not only allow of mixing without precipitation but would enable one to control the subsequent rate of reaction by a suitable regulation of the temperature.

Such a favorable combination of circumstances apparently obtains when a manganese salt of a strong acid and KH_2AsO_4 are mixed. The latter salt ionizes thus:

$$KH_2AsO_4 \rightleftharpoons K^{\cdot} + H_2AsO_4{}'$$

but on account of the solubility of $Mn(H_2AsO_4)_2$ no Mn ions are removed from solution by interaction with $H_2AsO_4{}'$. However the latter ion undergoes secondary ionization to a slight degree as follows:

$$H_2AsO_4{}' \rightleftharpoons H^{\cdot} + HAsO_4{}''$$

and insoluble $MnHAsO_4$ is formed in accord with the following reaction:

$$Mn^{\cdot\cdot} + HAsO_4{}'' = MnHAsO_4$$

Since the precipitation of $MnHAsO_4$ is accompanied by the formation of an equivalent amount of free hydrogen ion in solution an equilibrium is set up which prevents the complete precipitation of the manganese. However the amount of $MnHAsO_4$ formed and the rate of formation by the above process are apparently influenced to a marked degree by the temperature, so that we should be able to realize experimentally the conditions most favorable for the formation of a jelly by direct precipitation from solution.

Experimental

Ferric arsenate jellies. Colloidal ferric arsenate was prepared as described by Holmes and Arnold by adding ferric chloride in excess to a solution of N Na_2HAsO_4. 600 cc of the colloid containing the equivalent of 18 g $Fe_2(HAsO_4)_3$ was dialyzed in the cold with the Neidle dialyzer. If a considerable excess of $FeCl_3$ is not employed, the colloidal solution sets to an opaque yellowish white jelly on dialysis over night. With a large excess of ferric chloride prolonged dialysis was necessary to obtain a jelly which in this case was perfectly clear, firm and yellowish red in color. The red color is undoubtedly due to the presence of colloidal ferric oxide formed by hydrolysis of the chloride, as pointed out by Holmes.

A colloid prepared by mixing 400 cc of N $FeCl_3$ and 200 cc of N Na_2HAsO_4 was dialyzed for several days. 20 cc portions of the colloid were diluted to 40 cc and in them were suspended parchment thimbles containing 5 cc of electrolytes. The electrolyte diffused slowly through this parchment and precipitated the colloid. Observations were made after a considerable amount but not all of the solution was coagulated. The results are given in Table I.

TABLE I
Precipitation of Colloidal Ferric Arsenate by Electrolytes

Precipitant	Nature of precipitate
N Citric acid	Gelatinous precipitate; partly dissolved
0.1 N Citric acid	Jelly somewhat cloudy
0.01 N Citric acid	Clear jelly
N Phosphoric acid	Gelatinous precipitate; partly dissolved
0.1 N Phosphoric acid	Jelly somewhat cloudy
0.01 N Phosphoric acid	Clear jelly
0.1 N Sulphuric acid	Cloudy jelly
0.01 Sulphuric acid	Clear jelly
N Sodium sulphate	Cloudy jelly
0.1 N Sodium sulphate	Jelly somewhat cloudy
0.01 N Sodium sulphate	Clear jelly

The results recorded in Table I confirm the conclusion that ferric arsenate jellies may be formed by adding a suitable amount of precipitating electrolyte to the colloidal solution of the salt. If the concentration of the electrolyte within the membrane is too great the precipitation concentration is reached quickly near the surface of the membrane so that rapid precipitation takes place at once at this point and continues step-wise with the formation of a gelatinous precipitate. With a dilute solution the precipitation concentration is attained slowly throughout a considerable portion of the colloid and the uniform coagulation results in a jelly. It will be recalled that Holmes believed that jellies were formed by dialysis of ferric arsenate on account of the removal of H' ion and the consequent shifting to the left of the equilibrium represented by the equation

$$Fe_2(HAsO_4)_3 + 6\ HCl \rightleftarrows 2\ FeCl_3 + 3\ H_3AsO_4.$$

While it is true that HCl shows both a solvent and peptizing action on ferric arsenate, the latter is the only one of importance with low concentrations of acid. It would seem therefore that the reduction of the hydrogen ion concentration below a critical value was important largely because hydrogen ion happened to be the stabilizing ion. If this is the case then the addition of an electrolyte having a strongly adsorbed cation would neutralize the adsorbed hydrogen ion and so would have the same effect as decreasing the actual hydrogen ion concentration in solution. Indeed the hydrogen ion concentration in the solution might even be increased by the addition of an acid with a multivalent anion that is strongly adsorbed providing the solvent action of this acid is not too great. The accuracy of the conclusions is indicated by the results given in Table I. From the observations there seemed to be no necessary reason for adding the precipitating electrolyte slowly by diffusion through parchment. A suitable concentration of electrolyte added directly to the colloid should produce the same results. This was found to be the case as shown by the experiments recorded in Table II. To 5 cc of the colloid was added the amount of electrolyte shown in the first column in the table; observations were made after allowing the mixture to stand for the period of time noted in the third column.

TABLE II

Precipitation of Colloidal Ferric Arsenate by Electrolytes

Electrolyte added to 5 cc colloid	Final Volume cc	Time	Nature of precipitate
5 cc N/100 $H_2C_2O_4$	10.0	10 da	No precipitate
6 cc N/100 "	11.0	10 da	Partly precipitated, gelatinous
0.2 cc N/10 "	5.2	7 da	Perfectly clear jelly
0.3 cc N/10 "	5.3	4 da	Perfectly clear firm jelly
0.5 cc N/10 "	5.5	1 da	Firm opalescent jelly
0.6 cc N/10 "	5.6	1 hr	Firm opaque jelly
4 cc N/100 H_2SO_4	9.0	1 da	Perfectly clear jelly
6 cc N/100 "	11.0	1 da	Firm slightly opalescent jelly
8 cc N/100 "	13.0	1 da	Firm opalescent jelly
0.2 cc N/10 "	5.2	4 da	Perfectly clear jelly
0.4 cc N/10 "	5.4	3 da	Firm jelly; slightly opalescent
0.8 cc N/10 "	5.8	1 hr	Firm opaque jelly
1.5 cc N/10 "	6.5	2 min	Gelatinous precipitate
4 cc N/100 H_3PO_4	9.0	7 da	Perfectly clear soft jelly
6 cc N/100 "	11.0	7 da	Perfectly clear soft jelly
0.2 cc N/10 "	5.2	10 da	Perfectly clear soft jelly
0.4 cc N/10 "	5.4	4 da	Clear firm jelly
0.8 cc N/10 "	5.8	1 da	Firm very cloudy jelly
1.5 cc N/10 "	6.5	3 min	Gelatinous precipitate
0.1 cc N/10 Citric	5.1	7 da	Perfectly clear weak jelly
0.2 cc N/10 "	5.2	4 da	Perfectly clear firm jelly
0.4 cc N/10 "	5.4	3 da	Firm slightly opalescent jelly
0.6 cc N/10 "	5.6	1 da	Firm cloudy jelly
1.0 cc N/10 "	6.0	2 min	Gelatinous precipitate
2 cc N/100 NH_4OH	7.0	3 da	Perfectly clear weak jelly
3 cc N/100 "	8.0	1 da	Firm opalescent jelly
5 cc N/100 "	10.0	1 hr	Firm opaque jelly
0.1 cc N/10 "	5.1	3 da	Perfectly clear weak jelly
0.2 cc N/10 "	5.2	1 da	Perfectly clear firm jelly
0.5 cc N/10 "	5.5	1 min	Gelatinous precipitate
1 cc N/100 $NaC_2H_3O_2$	6.0	10 da	No precipitate
2 cc N/100 "	7.0	6 da	Perfectly clear soft jelly
3 cc N/100 "	8.0	3 da	Perfectly clear firm jelly
5 cc N/100 "	10.0	1 hr	Opaque jelly
0.2 cc N/10 "	5.2	4 da	Perfectly clear weak jelly
0.3 cc N/10 "	5.3	3 da	Perfectly clear firm jelly
0.5 cc N/10 "	5.5	1 da	Opaque jelly
1 cc N/100 Na_2SO_4	6.0	5 da	Perfectly clear soft jelly
1.5 cc N/100 "	6.5	3 da	Perfectly clear firm jelly
2 cc N/100 "	7.0	1 da	Firm slightly opalescent jelly
6 cc N/100 "	11.0	1 hr	Opaque jelly

The above results merely emphasize the importance of neutralizing the adsorbed stabilizing hydrogen ion since suitable acids, bases and salts are equally effective in the precipitation of a jelly from colloidal solutions. It will be noted that if too little electrolyte is added no jelly or an imperfect or soft jelly results while, if too much electrolyte is used, a gelatinous precipitate is obtained. All stages in the process from the formation of weak clear jellies through firm clear jellies and firm opalescent jellies to gelatinous precipitates can be realized by suitable variation in the amounts of the several electrolytes.

Aluminium arsenate jellies. Colloidal aluminium arsenate was prepared in the same manner as ferric arsenate and the nature of the precipitate on coagulation with electrolytes was observed. The procedure was similar to that described above. The observations made after four days, as given in Table III, confirm the result obtained with collodial ferric arsenate.

TABLE III

Precipitation of Colloidal Aluminium Arsenate by Electrolytes

Electrolyte added to 5 cc colloid	Final volume cc	Nature of precipitate
0.05 cc N/10 $NaC_2H_3O_2$	5.05	No precipitate
0.1 cc N/10 "	5.1	Firm clear jelly
0.15 cc N/10 "	5.15	Firm opalescent jelly
1.0 cc N/100 "	6.0	Firm clear jelly
2.0 cc N/100 "	7.0	Gelatinous precipitate
1.3 cc N/100 Na_2SO_4	6.3	Soft jelly
1.4 cc N/100 "	6.4	Soft jelly
1.y cc N/100 "	6.6	Gelatinous precipitate
0.4 cc N/100 NH_4OH	5.4	No precipitate
0.6 cc N/100 "	5.6	Soft clear jelly
1.0 cc N/100 H_2SO_4	6.0	No precipitate
2.0 cc N/100 "	7.0	Clear firm jelly
4.0 cc N/100 "	9.0	Clear soft jelly

Manganese arsenate jellies. In the previous section I pointed out that a necessary condition for the formation of dilute jellies by precipitation directly from solution was delay in the precipitation of a hydrous substance until thorough mixing of the interacting solutions was effected. When solutions of a manganese salt are mixed with a solution of dihydrogen arsenate the following reaction takes place.

$$H_2AsO_4' = HAsO_4'' + H^{\cdot}$$
$$Mn^{\cdot\cdot} + HAsO_4'' = MnHAsO_4$$

Since Diesz has shown that the amount of $MnHAsO_4$ precipitated and the velocity of the precipitation are greater the higher the temperature, it seemed desirable to bring about the mixing of the solutions at as low a temperature as possible and then warm the mixture to the temperature necessary to get adequate precipitation. The method of procedure was as follows: Solutions of ½ molar $MnCl_2$ and ⅓ molar KH_2AsO_4 were prepared from freshly boiled water. We found that this precaution was necessary in order to prevent the formation of air bubbles in the jelly. The solutions were cooled to 0° and measured amounts of each were placed in 60 cc test tubes in the ratio shown in the table. The solutions were diluted with cold water either to the final volume shown in column 3 of Table IV or to an aliquot part thereof. The water was distributed between the two test tubes so that the volume in each was the same. The mouths of the tubes were then connected with a piece of large thin rubber tubing used in connection with Gooch filter funnels. Rapid mixing was accomplished by inverting one of the tubes quickly and then promptly throwing the entire contents back into the empty tube. The mixture was set aside for 15-20 minutes, and if jelling had not begun, the tube was then warmed by dipping carefully into boiling water until precipitation started, after which it was allowed to stand quietly. In the experiments using KH_2AsO_4 it was possible in every case to get complete mixing before precipitation started and excellent clear jellies were obtained. With the secondary and tertiary salts instantaneous formation of a gelatinous precipitate or a cloudy heterogenous jelly was produced. The results are shown in Table IV.

TABLE IV

Precipitation of Manganese Arsenate

Electrolytes mixed cc		Final volume	Nature of Precipitate.
$MnCl_2$	KH_2AsO_4		
10	10	20	Firm jelly almost clear
10	20	30	Firm jelly almost clear
10	20	50	Firm jelly perfectly transparent
10	20	100	Firm jelly perfectly transparent
10	20	200	Soft jelly perfectly transparent
10	20	300	No jelly
	NaH_2AsO_4		
10	10	20	Cloudy jelly not uniform
10	10	50	Cloudy gelatinous precipitate

The manganese arsenate jellies prepared as above described are unusually clear and perfect and are very stable showing little tendency to cloud up and crystallize after standing a month; and they undergo little or no contraction or syneresis on standing.

On heating the jelly, crystals of $MnHAsO_4$ were formed. Diesz found that about half the theoretical amount of salt was precipitated on mixing solutions of $MnCl_2$ and KH_2AsO_4 in the approximate ratio given in Table III and heating the mixture for eight hours on the water bath. The amount of $MnHAsO_4$ formed under the conditions of our experiments was doubtless much less; but assuming that half the theoretical amount was precipitated, it follows that a very firm jelly results with 0.5% and a soft jelly with but 0.25% $MnHAsO_4$. Good jellies are not obtained by mixing $MnCl_2$ and Na_2HAsO_4 since the precipitation is instantaneous not allowing time for the formation of the jelly structure after the mixing.

Zinc arsenate jellies. Zinc arsenate jellies result on mixing zinc sulphate with KH_2AsO_4 or Na_2HAsO_4 under suitable conditions. The jellies formed with Na_2HAsO_4 were cloudy and not uniform because of too rapid precipitation. The precipitation was more rapid on adding KH_2AsO_4 to a solution of a zinc salt then to a manganese salt. Good jellies were therefore obtained only at fairly high dilutions which slowed down the precipitation and allowed time for mixing. It seemed likely that the same result could be accomplished with more concentrated solutions by increasing the hydrogen ion concentration slightly. This was true as shown by the observations recorded in Table V.

TABLE V

Percipitation of Zinc Arsenate

Solutions mixed cc		Final volume cc	Nature of precipitate
$ZnSO_4$	K_2HAsO_4		
10	10	20	Gelatinous precipitate formed at once enclosing most of the water. Cloudy.
10	20	30	Cloudy gelatinous precipitate formed at once enclosing all the water.
10	10*	20	No precipitate until after warming. Firm clear jelly
10	20	50	Gelatinous precipitate formed at once but mixture set to a fairly clear jelly that was not uniform and contained air bubbles.
10	20*	50	Excellent clear jelly.
10	10	40	Precipitation delayed slightly. Firm jelly slightly opalescent.
10	10	60	Perfectly clear transparent jelly.
10	20	100	No immediate precipitation. Perfectly clear jelly on warming.
	Na_2HAsO_4		
10	10	50	Immediate precipitation of cloudy jelly; not uniform

*0.1 cc N H_2SO_4 added before mixing.

The results recorded in Table V on the formation of zinc arsenate jellies emphasize the importance of preventing precipitation until mixing of the solutions is complete. From the observations one would predict that a gelatinous precipitate but not a jelly would form on mixing a zinc salt of a weak acid with KH_2AsO_4. This was tested with zinc acetate and the conclusion confirmed. Instantaneous precipitation of a cloudy gelatinous precipitate instead of a clear uniform jelly took place even with quite dilute solutions.

To obtain good zinc arsenate jellies it is necessary to control the conditions of precipitation more carefully than with manganese arsenate. Moreover the jellies are less stable and even the dilute one become cloudy in a few days owing to the formation of crystals.

Cadmium arsenate jellies. Cadmium arsenate tends to precipitate rapidly as a gelatinous precipitate which goes over quickly to a crystalline mass so that it is impossible to obtain jellies that will remain clear for more than a few minutes. If the hydrogen ion concentration is increased in an attempt to slow down the precipitation the solvent action causes the formation of a crystalline precipitate. The results of a series of experiments are given in Table VI.

TABLE VI

Precipitation of Cadmium Arsenate

Solutions mixed cc		Final volume cc	Nature of precipitate
$CdSO_4$	K_2HAsO_4		
10	10	20	Jelly starts to cloud up quickly
10	10	40	Gelatinous precipitate at outset setting quickly to semi-transparent jelly that starts to crystallize in a short time.
10	10	60	Similar to the preceeding but more stable
10	10* Na_2HAsO_4	20	Crystalline precipitate
10	10	50	Gelatinous precipitate

*0.05 cc N H_3AsO_4

The results confirm Klemp and Gyrlay's observations regarding the instability of cadmium arsenate jellies. The tendency of copper arsenate to form a granular precipitate is so great that it was not possible to precipitate it in the form of a jelly.

Cobalt arsenate jellies. Cobalt arsenate tends to precipitate in a gelatinous form and considerable difficulty was encountered in preparing a jelly. On mixing $CoCl_2$ and Na_2HAsO_4 precipitation was quite slow on standing at room temperature and a flocculent precipitate always resulted. To obtain a jelly the solutions were mixed and the container was dipped in boiling water to start precipitation and then allowed to stand quietly for a suitable period. Too little or too much heating always results in a flocculent precipitate instead of a jelly. The results are given in Table VII.

TABLE VII

Precipitation of Cobalt Arsenate

Solutions mixed cc		Final volume cc	Nature of precipitate
$CoCl_2$	KH_2AsO_4		
10	10	20	Firm cloudy rose-colored jelly
20	10	30	Firm cloudy rose-colored jelly
20	10	40	Firm cloudy rose-colored jelly
20	10 Na_2HAsO_4	50	Firm cloudy rose-colored jelly
10	10	50	Blue gelatinous precipitate

In every case the cobalt arsenate jellies were opaque but they were apparently uniform in structure and were quite stable.

Ferrous arsenate jellies. To prepare ferrous arsenate jellies a solution of ferrous ammonium sulphate was mixed with KH_2AsO_4 and the mixture allowed to stand quietly over night. The jellies formed slowly and the process could not be hastened by warming, since a gelatinous precipitate formed under these conditions. The results of a series of experiments are given in Table VIII.

TABLE VIII

Precipitation of Ferrous Arsenate

Solutions mixed cc		Final Volume cc	Nature of precipitate
$FeSO_4(NH_4)_2SO_4$	KH_2AsO_4		
10	10	20	Firm greenish jelly slightly cloudy
10	20	30	Firm greenish jelly slightly cloudy
10	20	80	Firm greenish jelly slightly cloudy

Summary

The results of this investigation are as follows:

1. Von Weimarn has shown that any sparingly soluble salt may be precipitated in the gelatinous form if the concentration of the reacting substances and so the percentage supersaturation is sufficiently great. These are however not the conditions under which jellies are usually formed and the amount of enclosed liquid is relatively small. The limitations of the von Weimarn generalization are discussed in so far as the formation of inorganic jellies is concerned and the general conditions are outlined for the formation of typical dilute jellies where the amount of enclosed liquid is relatively very great.

2. The jelly structure is made up of a network of minute particles that adsorb liquid strongly, hence jellies may be prepared by coagulating a colloidal solution of a highly hydrous substance at a suitable rate in the absence of an electrolyte that possesses an appreciable solvent action. The effect of salts on the formation of jellies is determined in large measure by the precipitating and stabilizing action of the ions in so far as these influence the amount and velocity of coagulation. A relatively slow rate of precipitation is essential such as may be realized in the immediate region of the precipitation concentration of an electrolyte. A little below this value no precipitation or only a slight precipitation takes place while above this value coagulation is usually so rapid that a gelatinous precipitate is formed instead of a jelly. The reason is that time is not allowed for uniform mixing of the colloid with coagulant and the slow uniform precipitation that is necessary for the building of a uniform jelly structure is replaced by rapid uneven coagulation and the consequent contraction that distinguishes a gelatinous precipitate from a jelly.

3. The formation of jellies by dialysis of a colloidal solution of a hydrous substance is a special case of coagulation of a colloid by decreasing the adsorp-

tion of the stabilizing ion below a critical value as a result of reducing its concentration in solution. The same result is accomplished by adding the right amount of electrolyte with a suitable precipitating ion the adsorption of which neutralizes the adsorption of the stabilizing ion.

4. Colloidal ferric arsenate and aluminum arsenate were prepared which owe their stability to adsorbed hydrogen ion. Jellies result by reducing the concentration of the stabilizing ions by prolonged dialysis. Similar results were obtained by coagulating the colloids with various electrolytes having strongly adsorbed cations, such as citric, sulphuric, phosphoric and oxalic acid and ammonium hydroxide, sodium sulphate and sodium acetate. Since jellies are formed by coagulation of the colloid by acids it is evident that the important thing is the neutralization of the adsorbed hydrogen ion and not the actual hydrogen ion concentration in the solution.

5. Jellies may be formed by mixing quite dilute solutions that react to form a hydrous precipitate providing the precipitation can be delayed until ~~the interacting solutions are thoroughly mixed and then can be made to pro~~ceed at a suitable rate. Immediate precipitation always results in the formation of a gelatinous or flocculent precipitate instead of a jelly.

6. The conditions stipulated in (5) were realized with the arsenates of Mn, Co, Fe$^{\cdot\cdot}$ Cd, and Zn by mixing solutions of their salts of strong acids with KH_2AsO_4 in the cold and allowing them to stand at room temperature or warming to a suitable temperature. The mechanism of the process is outlined and the importance of the temperature and the hydrogen ion concentration on the rate of precipitation and hence on the nature of the precipitate, is discussed.

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STUDIES ON THE FORMATION OF PERIODIC PRECIPITATES. II

BY N. R. DHAR AND A. C. CHATTERJI

In the first paper of this series[1] the following facts have been brought out:

Gelatine previously mixed with dichromate has a better peptising effect upon silver chromate than when it is previously mixed with silver nitrate. It is very likely that this has some bearing on the common practice of adding silver nitrate solution over that of gelatine and dichromate. We have also studied the peculiar behaviour of the products obtained by mixing together a metallic salt (capable of giving an insoluble hydroxide), ammonia or alkali hydroxide and glycerine or a concentrated solution of sugar. We get or do not get the precipitate of the hydroxide, according as we add the salt solution to a mixture of glycerine and alkali or the hydroxide to the mixture of glycerine and the solution of the salt. We have proved that these are real cases of peptisation. We have also observed that insoluble metallic hydroxides like those of iron or cobalt can be peptised not only in presence of glycerine or a concentrated sugar solution, but also in solution of gelatine, agar, gum arabic and even starch. It was also observed that the power of peptisation possessed by a certain amount of any of these substances depends a good deal upon the concentrations of the reacting solutions. Thus glycerine may not be able to peptise ferric hydroxide if a very concentrated solution of ferric chloride be used. It was also observed in that paper that the periodic precipitation produced when an electrolyte reacts upon another already dissolved in gelatine or agar seems to have a close connectioni n its action with the peptisation phenomenon noted above.

In this paper the effects of change of concentration of the reacting substances and of the gel have been investigated. Moreover the action of diffused daylight on the formation of Liesegang rings has been studied. Experiments have been conducted in diffused light of the laboratory and in the dark under identical conditions. A general explanation of the formation of periodic precipitate has also been advanced.

Numerous experiments were made with silicic acid gel containing sodium chloride as one of the reacting substances. Gels of three concentrations containing equivalent amounts of sodium chloride were used, the concentrations of silicic acid and of sodium chloride were widely varied in these three sets of experiments. In every case N/1 silver nitrate, N/2 silver nitrate and N/4 silver nitrate were allowed to diffuse in test tubes containing the gel and sodium chloride and experiments were conducted in light and in the dark. In the other series of experiments with the three different concentrations of the gel 30%, 20%, 10%, 5%, 2½%, and 1¼%, solutions lead nitrate was allowed to diffuse in test tubes containing silicic acid and sodium chloride.

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[1] N. G. Chatterji and N. R. Dhar: Kolloid-Z, 31, 13 (1922)

The following is the summary of results obtained with lead nitrate as the diffusing liquid:—

In all tubes the rings of lead chloride are very fine and close together at the top and as we go down the tube the rings get separated and the distance between two consecutive rings goes on increasing, at the same time the rings become more and more prominent and thicker and thicker. At the beginning the concentration of lead nitrate is high and consequently more lead chromate is formed and hence the solution of lead chromate has a much greater possibility of coagulation. Later on the concentration of the diffusing substance gradually falls off and hence the limiting concentration of the sol of lead chromate at which coagulation takes place is obtained after a sufficient interval. That is why the distance between the rings gets greater and greater as one goes down the tube.

2. By keeping the concentration of lead nitrate constant and decreasing the concentration of the gel and of sodium chloride to half and one fourth, the rings decrease in prominence by becoming finer and finer, i.e. with the decrease in the concentrations of the gel and of sodium chloride the actual amount of precipitate in a single ring at an equal distance from the precipitate decreases. The rings seem to become more and regular. The explanation is that the amount of lead chloride formed is less because the concentration of sodium chloride is also decreased.

3. By keeping the concentration of sodium chloride and of the gel constant and varying the concentration of lead nitrate solution, the following results are obtained:—

(a) The rings are clearly visible in all tubes; the width of the rings at an equal distance from the interface increases with the decrease in strength of the lead nitrate solution. This and the following facts can be explained on the basis of diffusion of lead nitrate and the falling off in the concentration of the salt as we go down the tube.

(b) The distance between two consecutive rings at an equal distance from the interface increases as the strength of lead nitrate is decreased i.e. the rings are less closely packed as the strength of lead nitrate is decreased.

4. By keeping the concentration of lead nitrate constant and varying the concentration of gel to half and to one fourth, the distance between two consecutive rings at the same distance from the interface decreases i.e. the rings are closely packed as the strength of the gel is decreased. This is due to the change in the concentration od the peptising agent. The less the concentration of the gel the greater is the possibility of coagulation.

5. The tubes are not affected by diffused light.

6. In some tubes alternate thick and thin rings are seen. By decreasing the concentration of the gel, tubes containing stronger lead nitrate solution contain thick and thin rings, while with sufficiently strong gel this is not observed.

The following results are obtained with silver nitrate as the diffusing liquid:—

1. By keeping the concentration of silver nitrate constant and varying the amount of silicic acid by half and one fourth, the length of continuous precipitate of silver chloride is increased. By decreasing the concentration of silicic acid the chances of coagulation are increased, that is why the length of the uniform precipitate is increased.

2. By keeping the concentration of the gel constant and varying the amount of silver nitrate by half and one fourth, the length of continuous precipitate is decreased. This can be satisfactorily explained on the basis of the falling off of the concentration of silver nitrate by diffusion.

3. By keeping the strength of silver nitrate constant and by decreasing the strength of the gel to half and one fourth, the number of the bands increases as well as they become more and more clear. The width of a single band at equal distance from the interface increases with the decrease in the strength of the gel. The explanation can be given on the basis that the less the concentration of the gel the greater the chance of coagulation of the sol.

4. By keeping the strength of the gel constant and decreasing the strength of silver nitrate to half and one fourth the number of the bands is also decreased as well as they become more and more faint. The width of a single band at equal distance from the interface decreases with the decrease in the strength of the silver nitrate solution. This is because of the fact that the greater the concentration of the gel the less the chance of coagulation of the sol.

5. In cases where the test tubes were exposed to diffused light, bands were developed with rapidity and were clearly visible while no rings were visible in majority of tubes kept in the dark, though the length of the diffused precipitate was the same. Silver salts are highly affected by light. It has already been said that light is a very good coagulating agent, that is why test tubes exposed to light develop bands with rapidity whilst a tube kept in the dark shows no bands. The bands are due to coagulated silver chloride.[1]

From our experiments we find that diffused light affects only the tubes containing silver chloride and silver iodide, whilst the rings of lead chloride and lead iodide in silicic acid are entirely unaffected by diffused light. These results are in harmony with those obtained recently by Liesegang[2] but are not in agreement with those obtained by Hatschek.[3]

It appears that almost all sparingly soluble substances are capable of forming Liesegang rings in a suitable gel.

With agar as the gel, experiments were performed in the dark and in the diffused light with the object of obtaining rings of lead iodide, mercuric iodide and silver iodide. With lead iodide there is absolutely no difference in the nature of the rings obtained in light and in the dark. Rings of mercuric iodide

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[1] Compare Ganguly and Dhar: Kolloid-Z. 31, 17 (1922)

[2] Kolloid-Z. 32, 263 (1923)

[3] Proc. Roy. Soc. 99, 496 (1921)

in agar were obtained by the interaction of mercuric nitrate and potassium iodide as well as by the interaction of mercuric chloride and potassium iodide. At first with mercuric iodide the rings are clearly formed when the concentrations of mercuric nitrate and potassium iodide are low. After the lapse of a few days the rings become quite prominent. When dilute solutions of mercuric chloride are allowed to react on potassium iodide, bands of mercuric iodide are formed which are alternately red and yellow. Those tubes which are exposed to diffused light show more rings than those in the dark. Silver iodide gave rings only in diffused light; no rings were visible in the dark.

A quantitative explanation of the formation of periodic precipitates is yet to come. The earliest one due to Ostwald assumes supersaturation followed by precipitation, and consequently clearing of the immediate neighbourhood of the precipitate from the reactants, so that the diffusing ion has to travel some distance before precipitation again occurs. Hatschek holds that this theory is disapproved by the fact that periodic precipitation still takes place in the presence of crystalline nuclei of the precipitate or of a previous stratification which should have rendered supersaturation impossible. It is well known that release of supersaturation takes place very readily or rather instantaneously when crystalline nuclei are added to a supersaturation solution. Innumerable centres of crystallisation are created and in a very short time the solution is freed from the extra amount of the dissolved substance.

It is practically certain that in presence of gelatine or agar or any other protecting colloid substances like silver chromate, lead chromate, lead iodide, etc., which form Liesegang rings are in the peptised condition. In other words silver chromate or lead iodide, etc., remain in a colloidal state.[1] From our experiences on colloidal matter we know that if some finely solid substance is present in a colloidal medium, sometimes the colloidal matter coagulates; but this process is extremely slow in comparison with the phenomenon of the release of supersaturation from a supersaturated solution. We have not been able to coagulate silver chromate sol protected by a large amount of gelatine by keeping it in contact with solid silver chromate even for several days. On the other hand it has been observed that a sol of antimony sulphide containing a little tartrate gradually coagulates on the moulds formed after a few days due to the presence of the tartrate. From the above considerations it becomes difficult to accept the explanation of Ostwald, but there is some truth in the explanation because it is certain that a nucleus always favours precipitation. The suggestion of the late Lord Rayleigh[2] is also beset with the same difficulties as the explanation of Ostwald. In this connection it would be of interest to note that Barger and Field[3] found that a supersaturated solution of saponarin was colloidal, and this substance did not crystallise on addition of crystals of saponarin.

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[1] Compare Williams and MacKenzie: J. Chem. Soc., 117, 844 (1920)

[2] Phil Mag., 37, 738 (1919)

[3] J. Chem. Soc., 101, 1397 (1912)

The most important alternative theory of periodic precipitation was advanced by Bradford.[1] According to him one of the reacting solutes is adsorbed by the layer of precipitate, the result being a zone practically free from it so that the clear space between the strata is at once accounted for. There are several difficulties of this theory, which seems very interesting. In a foregoing paper[2] it has been proved that freshly precipitated manganese dioxide is a very good adsorbent of electrolytes. Manganese dioxide adsorbs mainly the positive portion of the salt. It has been observed that when freshly precipitated and washed and air dried hydrated manganese dioxide is used as an adsorbent the amount of electrolyte adsorbed is only a few per cent of the total amount of the electrolyte taken. It has also been observed in another paper[3] that manganese dioxide in the course of its formation is certainly a better adsorbent than the air dried specimen. Even then from our experiments we have repeatedly seen that manganese dioxide in the course of its formation adsorbs only a portion of the total amount of the electrolyte taken from substances like $AgNO_3$, $CdCl_2$, $CdSO_4$, $MgSO_4$, $MgCl_2$, etc. We have also observed that substances like barium sulphate hardly adsorb electrolytes like $CuCl_2$, $CuSO_4$, etc. Similarly freshly precipitated $Fe(OH)_3$ has been found to adsorb only a fraction of caustic potash or caustic soda even from a dilute solution. We have also observed that freshly precipitated Ag_2CrO_4hardly adsorbs any potassium chromate even from a dilute soultion. In view of these facts it is very difficult to accept the beautiful explanation suggested by Bradford of periodic precipitation. To prove the validity of this theory we must show that substances like $PbCrO_4$, PbI_2, Ag_2CrO_4 etc., can adsorb considerably electrolytes like potassium chromate, potassium iodide, etc., which is not corroborated by direct experiments on adsorption.

It is a great pity that the explanation of Ostwald or of Bradford leaves the gel which is certainly an important factor in periodic precipitation out of account altogether. Consequently the suggestions advanced so far to explain periodic precipitation seems to be unsatisfactory.

We have repeatedly observed that freshly precipitated $BaSO_4$ can adsorb various colloidal substances and the colloidal matter gets coagulated and settles down along with the barium sulphate. Thus sols of antimony sulphide, ferric hydroxide, cadmium sulphide silver iodide, silver bromide, etc. can be more or less readily coagulated by freshly pptd barium sulphate. Similarly ferric hydroxide has been found to precipitate several colloids, like ferric hydroxide sol barium chromate sol etc. Similarly solid lead chromate can readily coagulate a colloidal sol of lead chromate. Moreover it has been observed that freshly precipitated lead iodide and lead chloride can appreciably adsorb and coagulate the sols of lead iodide and lead chloride. Freshly precipitated sulphides of silver mercury and lead have been found to adsorb and coagulate the sols of the respective substances.

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[1] Biochem. J. **10**, 169 (1916); **11**, **14**, 157, (1917)

[2] N. G. Chatterji and N. R. Dhar: Kolloid-Z. **33**, 18 (1923)

[3] Ganguly and Dhar: J. Phys. Chem. **26**, 836 (1922)

If a little gelatine is added to the sols they become more stable and their coagulation becomes more difficult by the freshly pptd substances, just as coagulation of sols by electrolytes can be hindered by the addition of protective colloidal like gelatin, gum arabic, etc. In a similarly way the foregoing sols can be made more stable by the addition of protective colloids like gelatin, gum arabic, etc., against their precipitation by freshly precipitated substances like barium sulphate, lead chromate, lead iodide and lead chloride, etc.

The protecting substance surrounds the sol completely and forms an envelope round a particle of the sol in question and thus stops the intimate contact of the sol particles with the precipitating substance such as an electrolyte or barium sulphate. In our opinion this is the best explanation for the protecting action of substances like gelatin and gum arabic, etc., on sols in general.

From some preliminary experiments we find that a sol of antimony sulphide cannot be precipitated by freshly precipitated antimony sulphide though freshly precipitated barium sulphate can readily coagulate a sol of antimony sulphide. Similarly we could not coagulate a sol of silver chromate by freshly precipitated silver chromate but in majority of cases we have found that sols can be more or less completely coagulated by the respective solids in a freshly precipitated condition.

Basing on these observations we suggest the following explanation of the formation of Liesegang rings:—

Let us take the case of lead nitrate which is allowed to diffuse in a mixture of potassium chromate and agar. When lead nitrate comes in contact with potassium chromate in presence of agar, lead chromate and potassium nitrate are formed, the agar exerts a peptising influence on the lead chromate and at the beginning the substance remains in a more or less colloidal condition. On the other hand, the potassium nitrate is exerting a coagulating influence on lead chromate all the time. Now at the beginning the concentration of lead nitrate being high, the lead chromate formed is much in excess to that which the agar can hold in suspension and the lead chromate coagulates and this process is certainly facilitated by the other product of reaction, which is potassium nitrate in this case. The potassium nitrate is certainly partially adsorbed by the pptd lead chromate. The lead nitrate is continually diffusing and is passing through the precipitated layer of lead chromate by which a small quantity of lead nitrate is being adsorbed. The diffusing lead nitrate is coming in contact with lower layers of potassium chromate and is at first forming colloidal lead chromate in presence of the protective agent, agar. This colloidal lead chromate is gradually coagulated by the solid lead chromate already formed and settles on the solid; in this way a layer next to the solid becomes free from lead chromate sol. The diffusing lead nitrate passes through this layer which is practically free from chromate and comes in contact with another layer of potassium chromate and at first it forms a layer of colloidal lead chromate but gradually the concentration of lead chromate increases and the colloidal matter gets coagulated; this process is facilitated by the presence of potassium nitrate. This explanation seems satisfactory in cases where the colloidal matter has been found to be coagulated by the presence of the solid. We have observed that solid lead chromate can adsorb and coagulate colloidal lead chromate. In those cases in which coagulation of sol cannot take place in presence of the solid matter, the explanation becomes more complicated. In these cases it seems likely that the second product of the reaction e.g. potassium nitrate formed by the interaction say of mercuric nitrate and potassium iodide, plays a dominant part in the process of coagulation. From the experiments of Linder and Picton and others we know that substances like antimony sulphide, are readily coagulated by electrolytes and appreciable quantities of the electrolyte are adsorbed by the precipitate. It is quite likely that mercuric iodide which exists in the beginning in a more or less colloidal condition gets precipitated due to the presence of the electrolyte, say potassium nitrate, and a part of the potassium nitrate is adsorbed by the precipitate. Consequently the layer next to this precipitate contains much less of the precipitating agent and hence a layer of mercuric iodide can exist in the peptised condition without coagulation taking place. The diffusing mercuric nitrate might pass through this layer and will react with a fresh layer of potassium iodide. The mercuric iodide thus formed will gradually coagulate under the influence of potassium nitrate and by its concentration becoming too large to remain in the peptised condition. This case is fundamentally different from the previous one already discussed. In this case we get a layer of coagulated mercuric iodide followed by a layer of colloidal mercuric iodide and soon, whilst in the former case we ought to get a layer of pptd. lead chromate followed by a zone practically free from lead chromate and so on. These conclusions are extremely interesting in light of the following observations by Hatschek[1]. Only in a few reactions, of which the original silver chromate one is the best example, are the clear spaces between the rings practically free from the insoluble compounds. In most cases the rings contain a large number of small and the clear space a small number of large crystals or crystalline aggregate. A striking microscopic illustration is afforded by cadmium sulphide in silicic acid gel, which exhibits no clear spaces at all but a continuous succession of alternately yellow and pink bands." In view of the suggestion advanced in this paper it is likely that solid cadmium sulphide cannot coagulate a sol of the same substance and the coagulation is effected by the electrolyte which is a product of the reaction. One of the bands is really due to coagulated cadmium sulphide and the precipitate in the process of coagulation has adsorbed a portion of the precipitating electrolyte making the next layer partially free from the coagulating agent, hence the next layer is likely to consist of cadmium sulphide in the colloidal state having a different colour.

Consequently the views advanced in this paper can satisfactorily explain two distinct classes of Liesegang rings. In one class a layer of precipitate is followed by a zone practically free from the sparingly soluble substance and

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[1] British Association Reports on Colloids, p. 23, (1919).

in such cases it is likely that the precipitate is capable of coagulating its own sol. The other class of rings consists of alternate layers of rings of different colours containing practically the same amount of insoluble substance in two successive layers. In this case the rings consist of a layer of coagulated sol followed by a layer of the peptised sol.

It will be extremely interesting to find out whether those substances in the solid state which can coagulate their own sols can only give rings of the first type, whilst incapable of coagulating their respective sols could give rings of the second class.

We are of the opinion that all sparingly soluble substances under convenient conditions and in suitable gels would be capable of forming Liesegang rings. Almost all sparingly soluble substances can be peptised by suitable concentrations of protecting substances like gelatine, agar, starch, etc. These peptised substances would be adsorbed and coagulated by their respective solids or they would be coagulated by electrolytes which are products of the chemical changes involved. Hence there is the possibility of the formation of Liesegang rings with almost all sparingly soluble substances under suitable conditions. Experiments on these questions are in progress in these laboratories. We have seen that with agar as gel and if a dilute solution of mercuric chloride is allowed to diffuse in a solution of potassium iodide bands of mercuric iodide are formed which are alternately red and yellow. It is very likely that the red bands are due to coagulated mercuric iodide, while the yellow bands are really peptised mercuric iodide. Direct experiments support the above conclusions. A tube containing yellow and red layers of mercuric iodide in gelatine was cut near the yellow layer, which was treated with hot water and a clear solution was obtained. The clear solution immediately gave a black precipitate when H_2S was added to it.

The yellow layer was very soft to the touch and looked like an amorphous substance, whilst in the red layers beautiful needle-shaped crystals were visible to the naked eye. The red layers were gritty to the touch because of the presence of crystalline mercuric iodide in these layers. Mercuric iodide can be readily peptised by gelatine and the peptised mercuric iodide has a yellow colour.

It has been found in several cases that in presence of diffused light, more numerous bands are found than in the dark. The explanation is pretty simple. In a foregoing paper[1] we have proved that light is a very good coagulating agent, hence in diffused light there would be more of coagulation of substances like mercuric iodide, lead iodide, etc., from the peptised condition than in the dark, consequently, in general more numerous rings are formed in diffused light than in the dark.

It is interesting to observe that in the case of silver chromate in gelatine and in several other cases, rings are formed in a liquid medium. Moreover in several cases rings were formed on the sides of the test tube above the surface of the liquid, strata appearing for several millimeters on the glass walls of the tube.

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[1] Ganguly and Dhar: Kolloid-Z. 31, 17 (1920)

Williams and Mackenzie (loc. cit) have studied the conditions of the precipitation of silver chromate in gelatine. They allowed to diffuse solutions of silver nitrate or potassium chromate in gels already containing silver chromate and in all cases they obtained stratification and they have drawn the following conclusions from these experiments:—"This means that in some manner or other the gel beneath a stratum of precipitate was cleared of the silver chromate. Whatever the cause, diffusion must have occurred to clear so perceptible a space. In other words, the silver chromate did not function as a colloid with a slow rate of diffusion." The above conclusions seem to be unsatisfactory as in presence of gelatine the silver chromate must be in the peptised condition. From the explanation advanced in this paper these results of Williams and Mackenzie would be clear. The precipitate of silver chromate at the interface will adsorb and coagulate the silver chromate sol next to it hence there would be a clear space free from silver chromate next to the precipitate. The diffusing silver ion or chromate ion from the top will pass through this layer which is free from silver chromate and will come in contact with silver chromate already existing in the next layer and when the concentration of silver chromate exceeds the maximum limit which can remain in the peptised condition, silver chromate will coagulate. This explanation seems to be quite satisfactory and on this view it is not necessary to imagine that silver chromate does not function as a colloid. Williams and Mackenzie have found that 860 grams of gelatin can keep a gram equivalent weight of silver chromate in the peptised condition. Yet they conclude that the precipitation of silver chromate occurs according to the usual rules of the solubility product and that the gel incidentally provides mechanical support for the precipitate. These conclusions seem to be untenable. We know that substances like silver chloride, silver chromate, etc., dissolve in ammonia, potassium cyanide, etc., due to the formation of complex salts which can give out in solution very few silver ions.

In general a sparingly soluble substance dissolves and remains in solution when there is the possibility of the formation of a complex substance. We have proved experimentally in a foregoing paper[1] that substances like ferric hydroxide, cobalt hydroxide, etc., readily pass into the peptised condition in presence of gycerine, concentrated sugar solution, starch, gelatin, agar and other protective colloids. Hence it is difficult to understand why a sparingly soluble substance like silver chromate will remain in a dissolved state in water containing gelatin. Real solution would have been possible if a complex salt could be obtained from silver chromate and gelatin but it is well known that no complex formation takes place in such cases. Consequently we are forced to the conclusion that silver chromate remains in the peptised or colloidal state in gelatin and the rate of diffusion of the substance in the peptised state must be very small.

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[1] Chatterji and Dhar: Trans. Faraday Soc. 16, 122 (1921)

The general theory advanced in this paper on the formation of two distinct classes of Liesegang rings seems to be applicable to all cases and marks an advance in the explanation of this phenomenon.

Summary and Conclusion

1. Gelatine previously mixed with dichromate has a better peptising effect upon silver chromate than when it is previously mixed with silver nitrate

2. In the formation of lead chloride rings in silicic acid gel by the interaction of lead nitrate and sodium chloride the rings are closely packed as the concentration of the gel is decreased. When other things are constant the rings are less closely packed as the strength of lead nitrate is decreased.

3. In the formation of silver chloride rings in silicic acid, similar results are obtained. Rings of silver chloride and silver iodide are affected by diffused daylight, whilst those of lead chloride and lead iodide are unaffected by light.

4. Tubes containing mercuric iodide rings when exposed to diffused daylight show more rings in light than in dark.

5. The theories explaining the formation of Liesegang rings developed by Ostwald and Bradford are found to be unsatisfactory.

6. We have found that in several cases, sols can be more or less completely adsorbed and coagulated by respective solids in a freshly precipitated condition. Basing on the above observations a theory of the formation of Liesegang rings in which a layer of coagulated matter is followed by a space free from the substance, has been advanced.

7. Mercuric iodide rings in gelatine, agar, etc., consist of a layer of coagulated and crystalline mercuric iodide which is red followed by a layer of colloidal mercuric iodide which is yellow. An explanation of the formation of the rings consisting of a layer of coagulated and crystalline matter followed by a layer of the peptised substance has been advanced, in which the adsorption of the second product of the chemical change is the dominant factor. It has been emphasised that there is the possibility of the occurrence of two distinct classes of Liesegang rings. In one class a layer of precipitate is followed by a zone practically free from the substance, whilst in the other case, the rings consist of a layer of coagulated sol, which in course of time might become crystalline, followed by a layer of the peptised sol.

8. We are of the opinion that all sparingly soluble substances under convenient conditions and in suitable gels would be capable of forming Liesegang rings.

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THE INFLUENCE OF GUM ARABIC ON THE HYDROLYSIS OF METHYL ACETATE

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The influence of temperature, of hydrogen ions, and of catalysts in general upon the velocity of hydrolytic processes is well known. Numerous theories have been put forth to explain the mechanism of catalytic reactions. The one of chief moment in so far as the present paper is concerned is the radiation hypothesis.

Arrhenius[1] assumed an equilibrium between active and inactive molecules of the substance catalyzed. A rise in temperature or the addition of a catalyst merely shifts this equilibrium in such a way as to increase the concentration of the active form. He expressed the relation between the change in the velocity coefficient of the reaction and the temperature by means of the expression:

$$\frac{d\log K}{dT} = \frac{E}{RT^2},$$

where E is the energy required to transform one mol of the substance from the inactive to the active state. Using thermodynamics and the theory of probability Marcelin[2] has deduced a relation for the effect of temperature which is identical with that of Arrhenius. He treats of the effect of temperature as a purely physical one and assumes that an inactive molecule becomes active when its internal energy is made to exceed a definite critical value. Lewis and Lamble[3] suggest that the E of Marcelin and of Arrhenius be called the "critical increment," since E represents the amount of energy which must be absorbed above the average value possessed by all of the molecules before the molecules become reactive. The source of this energy increment is to be found in the infra-red radiations of the system. Briefly stated the radiation theory is this. A substance becomes a catalyst when it can absorb infra-red radiations and then emit the energy in such waves or quanta as can be absorbed by the reactant, thus raising the internal energy of a number of molecules to the critical value. Nine papers contributed by Lewis and his co-workers[4] give experimental evidence which support this view. Tyndall[5] has found that gum arabic absorbs infra-red radiations. If it emits infra-red radiations which can be absorbed by methyl acetate, then gum arabic should, according to this theory, prove a powerful catalyst for methyl acetate.

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[1] Arrhenius: Z. phys. Chem., **4**, 22 (1889); **28**, 317 (1899).

[2] Marcelin: Compt. rend., **158**, 161 (1914).

[3] Lewis and Lamble: J. Chem. Soc., **105**, 2330 (1914).

[4] J. Chem. Soc., **105**, 2330 (1914); **107**, 233 (1915); **109**, 55, 67 (1916); **111**, 389, 457, 1086 (1917); **113**, 471 (1918).

[5] Tyndall: "Fragments of Science", "Radiant Heat and its Relations".

The original object of this research was to determine whether or not gum arabic will catalyze the hydrolysis of methyl acetate as the radiation theory predicts. It became evident very early in the work, however, that gum arabic is not a catalyst for this reaction. We proceeded therefore to study the influence of the gum upon the velocity of hydrolysis of methyl acetate when catalyzed by hydrochloric acid.[1]

The methyl acetate used was an exceptionally pure sample furnished by the Eastman Kodak Co. It was twice fractionally distilled and only the constant boiling middle portion was retained. The gum arabic was carefully selected from a large sample of practically pure white "tear gum". It was first finely ground in an agate mortar and then dried to approximately constant weight at 110°. An approximately 0.02 N solution of barium hydroxide was used in titrating the free acid. It was repeatedly checked against benzoic acid made from toluene. The acid was first resublimed and then kept for a short time slightly above the melting point to insure the removal of volatile impurities; it was then cast in sticks and carefully preserved. Phenolphthalein was the indicator used throughout the work.

All of the solutions and the reaction mixtures were prepared from freshly made conductivity water. All flasks, pipettes and burettes were previously certified by the Bureau of Standards. The temperature of the large water bath was accurately controlled to 25°±0.03.

In making up the reaction mixtures the gum was first added to the pure water and shaken until completely dissolved. Sufficient acid and water were then added to bring the solution to volume at the acid concentration desired, and the whole thoroughly shaken. These mother solutions and the pure ester were kept at 25° in the water bath. 50 c.c. portions of these solutions were transferred to tightly stoppered glass bottles, 2 c.c. of the ester was quickly added and the mixture vigorously shaken. The time of adding the ester was accurately noted. At stated intervals exactly 5 c.c. portions of the reaction mixture were transferred to 50 c.c. of ice-cold conductivity water and quickly titrated.

The values for the equilibrium constant were calculated by means of the equation:

$$K = \frac{2.303}{t_n - t_0} \log_{10} \frac{T_\infty - T_0}{T_\infty - T_n}$$

where T_0, T_n and T_∞ represent the number of c.c. of barium hydroxide solution necessary to neutralize 5 c.c. of the reaction mixture at times t_0, t_n and t_∞, respectively. In order to obtain the exact titration value, T_0, we plotted the values of $\log(T_\infty - T_n)$ as ordinates against the values of t as abscissae. The value of $\log(T_\infty - T_0)$ was then found by extrapolation.

Repeated series of experiments extending over many days were first made in which besides water and ester there were present 0.25, 0.5, 1.0 and

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[1] Owing to the fact that the junior author is leaving the University for a time the present paper is submitted as a preliminary report.

2.0 grams of gum arabic. These were compared from time to time with blank experiments run simultaneously and involving only water and ester. In no case did we find an appreciable increase in the velocity of hydrolysis.

Since the gum is not of itself a catalyst we next undertook to determine what influence, if any, the gum might exert upon the velocity of hydrolysis when the reaction is catalyzed by hydrochloric acid. The experimental method has already been described. Although the solutions containing one and two grams of gum arabic per 50 c.c. are quite viscous the constants are easily reproducible. The values for the velocity coefficients are collected in Table I. Each value is the mean of the values obtained for at least two different experiments. For the sake of comparison the velocity coefficients for solutions containing C mols of acid per liter and 0.0, 0.25, 0.50, 1.0 and 2.0 grams of gum arabic in 50 c.c. of the acid are given in Table II.

TABLE I

Influence of Gum Arabic upon the Velocity Coefficients of the Hydrolysis of Methyl Acetate

C. Acid	Gum. grams.	$K \times 10^5$	pH
0.020548	0.00	22.25	1.50
	0.50	13.52	1.80
	1.00	12.39	2.06
	2.00	10.94	2.67
0.041096	0.00	31.60	1.30
	0.25	28.96	1.41
	0.50	25.50	1.48
	1.00	23.37	1.56
	2.00	16.17	1.83
0.082190	0.00	55.91	1.15
	0.25	52.21	1.17
	0.50	51.75	1.19
	1.00	44.80	1.21
	2.00	36.67	1.25

TABLE II

A Comparison of the Velocity Coefficients

Gum (gr.)	0.00	0.25	0.50	1.00	2.00
C (acid)			$K \times 10^5$		
0.020548	22.25	....	13.52	12.39	10.94
0.041096	31.60	28.96	26.01	23.37	16.12
0.082193	55.79	52.81	51.87	46.17	36.89

A survey of these tables shows at once that gum arabic is not only not a catalyst for methyl acetate, but that by its presence the gum actually decreases the reaction velocity when catalyzed by hydrochloric acid. Furthermore, the velocity coefficients decrease as the concentration of the gum is increased, being more rapid in the dilute acid mixtures.

Speculation as to the influence of the gum upon the reaction velocity would obviously lead to two possible views. First, owing to its hydrophile nature the gum will adsorb water from the system and thus increase the concentration of both the ester and the acid. In turn there should be an increase in the velocity coefficients with an increase in the concentration of the gum. The results obtained are directly opposed to this view. Second, the gum will adsorb either the ester or the acid and thus decrease the activity of the molecular species adsorbed. The result in this case will lead to a decrease in the reaction velocity and such is actually the case.

While the time available was not sufficient to carry out an elaborate series of experiments on the influence of gum arabic upon the activity of the hydrogen ion, we thought it worth while to determine the pH values for the solutions used. These will give us qualitatively at least an idea of the influence of the gum upon the concentration of the hydrogen ion. Accordingly, solutions were prepared containing the identical proportions of acid and gum as used in the hydrolysis experiments. The pH values at 25° were determined precisely according to the method of Clark[1]. The values obtained are given in the fourth column of Table I. It will be observed that the pH values for each acid concentration increase as the concentration of the gum is increased, indicating a corresponding decrease in the effective concentration of the hydrogen ion. Moreover, the relative influence of the gum both on the velocity coefficients and on the pH values is greater in the more dilute acid solutions. This is in harmony with the well known adsorption phenomenon, viz., the adsorption of a solute by an adsorbent is relatively greater in dilute than in concentrated solutions. Apparently, therefore, gum arabic retards the catalysis of methyl acetate by hydrochloric acid by adsorbing the catalyst.

Summary

While gum arabic absorbs infra-red radiations it does not act as a catalyst for methyl acetate. Gum arabic retards the velocity of hydrolysis of methyl acetate when catalyzed by hydrochloric acid. Experimental evidence in the form of pH values leads to the conclusion that the gum adsorbs the catalyst.

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[1] Clark, "The Determination of Hydrogen Ions."

MISCELLANEOUS NOTES ON GAS KINETICS

BY S. C. LIND

The object of the present paper is to describe some experiments made several years ago which have remained unpublished on account, either of their uncompleted condition, or of the negative character of the results in one case. The recent trend of chemical kinetics appears to lend some interest to them either as suggestive of profitable directions of further research or possibly to spare others unnecessary experimental duplication.

1. Photo-sensitivity of a Hydrogen-Bromine Mixture at Higher Temperatures

Reaction tubes of the Victor Meyer type, about 8 cms long, 2 cms in diameter, of 25 cm³ volume, containing $\frac{1}{2}$ atmosphere (N. T. P.) each of H_2 and Br_2 were exposed at 250°C in a colorless vapor bath to the light from a 5 ampere - 110 volt carbon arc lamp. The reaction tube and arc lamp were both in the vertical position, 10 cms apart. It was found under these conditions that hydrogen and bromine combine at a rate 12 times that of the dark thermal reaction[1] at the same temperature. Kastle and Beatty[2] had previously shown in a qualitive way that at 196° C, H_2 and Br_2 combine in sunlight much more rapidly, than in the dark, and that even in diffused day-light the increase in rate was quite marked.

The character of the experiments of Kastle and Beatty would hardly justify their use for quantitative calculation, and the promised fuller report by them did not appear. Consequently, the writer is prompted to use his results at 250° C for some consideration in connection with the Nernst[3] theory of the excessive reaction between H_2 and Cl_2 from the standpoint of the Einstein[4] photochemical equivalence law. Nernst postulated that the wave lengths capable of absorption by Cl_2 gas would liberate Cl atoms, which would take part in a cyclical reaction with H_2 through the two partial steps:

$$Cl + H_2 = HCl + H + 25000 \text{ cals.}$$

$$\text{and} \quad H + Cl_2 = HCl + Cl + 19000 \text{ cals.}$$

Nernst assumed that on account of the positive heat of reaction of both steps this cycle would be spontaneously repeated a large number of times, thus accounting for the observed excess of a million fold over the requirements of the Einstein photochemical law.

Nernst further stated that the well known photo-chemical inactivity of $H_2 + Br_2$ is due to the fact that one step in the $H_2 + Br_2$ cycle has a negative heat of reaction and therefore does not take place spontaneously, namely: $H_2 + Br = HBr + H - 15{,}000$ cals.

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[1] Bodenstein and Lind: Z. phys. Chem. 57, 168 (1907).

[2] Kastle and Beatty: Am. Chem. J. 20, 159 (1898)

[3] Nernst: Z. Elektrochem., 24, 335 (1918)

[4] Einstein: Ann. Physik, (4) 37, 832; 38, 881 (1912)

Since, however, the H_2+Br_2 reaction does become light-sensitive at higher temperatures, as shown by Kastle and Beatty and by the present paper, one of three conclusions seems necessary: (1) The heat of reaction of the step H_2+Br may change so as to become + at 250°. A thermodynamic calculation based on the data of Lewis and Randall[1] for free energy and entropies based on the third law indicates that this can not be the case. This leaves open only the other two possibilities[2]: (2) that the Nernst "multicyclical" hypothesis is not correct or (3) that the H_2-Br_2 reaction under the conditions of the experiment does not exceed the requirements of the Einstein law, and therefore no multi-cyclical hypothesis is required. A rough calculation based on the experiment reported above for H_2+Br_2 at 250°, indicates that the rate of reaction observed will not exceed the photo-chemical equivalence, no matter what assumptions are made as to absorption efficiency and other influencing factors, and hence the Nernst hypothesis is not violated by the H_2+Br_2 reaction.

The fact, however, that the Nernst principle is not violated in the Br reaction does not, by any means, constitute a proof that it is true in the H_2+Cl_2 reaction[3]. In fact, it would be difficult to reconcile it with an observation attributed by Kastle and Beatty (loc. cit.) to Amato, that H_2 and Cl_2 at −12° C may be exposed for hours to direct sunlight without combination taking place. It is entirely improbable that the heat of reaction of either of the partial reactions involved in the interaction of H_2 and Cl_2 can change from a high positive to a negative value in the temperature interval of +20° to −12° C. A thermodynamic calculation similar to the one used for the H_2+Br_2 reaction does not indicate much change in velocity in this interval. This leaves then only the choices either that the absorption diminishes so that there is no primary atomisation at −12°, or the Nernst mechanism or Amato's observation is incorrect. It seems for several reasons that the latter is the case. In the first place, we do not in general find photochemical reactions to have high temperature coefficients. The use of the Bunsen and Roscoe actinometer involving an aqueous system has not permitted of wide variation of temperature, but the data available[4] do not show values that would explain Amato's result. Bodenstein and Dux[5] worked in a non-aqueous system and reported that within their limited range, temperature had little or no influence. It therefore appears that the observations of Amato at −12° must have been due to the presence of O_2 or some other inhibitor. However, in view of its important bearing on the Nernst hypothesis, the temperature co-efficient of the H_2+Cl_2 reaction ought to be made the subject of further investigation.

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[1] Lewis and Randall: "Thermodynamics" pp. 464 and 607 (1923)

[2] There is another possibility which does not particularly concern the Nernst hypothesis. The absorption of bromine may increase with temperature so that the necessary atomization first takes place at a temperature above the ordinary. This would furnish an additional reason for the absence of interaction between bromine and hydrogen at ordinary temperature and would throw no doubt upon the Nernst hypothesis, meaning simply that no bromine atoms would be present and that no cyclical reaction would take place even if they were.

[3] See note at end of this paper.

[4] M. Padoa: Gazz. chim. ital. 51I, 193 (1921)

[5] Bodenstein and Dux. Z. phys. Chem. 85, 306 (1913)

2. Activation of a H_2+Cl_2 Mixture for Thermal Reaction

In the course of some experiments with electrolytically generated H_2+Cl_2 mixture it was observed that the thermal reactivity increases progressively to a remarkable degree with the continued generation from HCl solution. This is quite similar to the well known increase of photo-chemical activity of such mixture, and suggests that the inhibitors for the thermal and the photochemical reactions may be identical in nature, as well as the reaction mechanism in both cases.

3. Attempt to arrest the Propagation of an Explosion in a Gas Mixture by an Electrical Field

The following experiment was made about 12 years ago under the impression that flame propagation is perhaps maintained by electron emission in the flame front and that if the electrons could be removed from the field of action by the imposition of an electrical field, the flame might be arrested. The advances made since that time in the theory of flame propagation as well as in electronics, would perhaps, not justify the experiment to-day, but it will nevertheless be briefly described in hopes that the negative result may have some interest in other connections.

A straight glass tube about 1 meter long and 1.5 cms internal diameter, closed with ordinary glass connections and stop-cocks at both ends, was cut in the middle so that a brass section about 10 cms long, of the same bore could be inserted. This was accomplished by means of a close-fitting glass sleeve over the outside of the joints, made gas-tight by Khotinski cement. The tube was mounted horizontally and an ordinary thin steel knitting needle was used as a central axial electrode through the brass section. The needle projected out into the glass tubes at both ends where it was centered and electrically insulated by resting on thin glass legs. To one end of the needle was fastened a platinum wire which was sealed through the glass tube to connect with one pole of a Wimshurst machine, the other pole being connected to the brass section of the explosion tube. A platinum spark gap was placed at one end of the tube to ignite the gases.

Electrolytic $2H_2+O_2$ mixture, generated from NaOH solution was introduced into the tube and brought to any desired pressure by means of a manometer. The pressure was first ascertained at which an explosion flame would just pass through the tube without a field. The explosion mixture was then introduced at a pressure somewhat above this critical value, the field was applied, the mixture sparked, and by observing in a dark room, one could easily see whether the flame traveled the entire length of the tube or stopped on reaching the brass section where the field was applied.

The first experiments served to indicate that the flame could be arrested at pressures as much as 25 mms above the critical explosive pressure. The results, however, were illusory owing to two factors:

(1) Moisture on the walls from previous combustion.

(2) Thin sparks or silent discharge in the brass section previous to the explosion caused premature impoverishment of the mixture by substitution of water vapor. It was finally concluded that the flame is not arrested by an electrical field. However, the source of voltage was not satisfactory. If the experiment were repeated at all, it should be with a more steady source of potential.

The only two observations that appear of possible interest were:

(1) That one can easily detect the difference between the bright yellow Na flame in H_2 and O_2 generated from NaOH or of the pale violet K flame in H_2 and O_2 from KOH solution, even when the H_2+O_2 mixture has been washed through H_2SO_4 solution, through several inches of closely packed cotton, and also allowed to stand in a gasometer for several weeks before use.

(2) Even below the explosive pressure, a H_2+O_2 mixture will be caused to combine rapidly by continued sparking. Since the energy supply to maintain sparking is much smaller than that to maintain incandescent glow to a wire or wire-net system it is possible that a sparking system might be used instead of a glow system to keep explosive gases from accumulating in switch-boxes,[1] city sewer systems or even in certain parts of mine workings.

I am indebted to Dr. D. C. Bardwell for his kind assistance with the calculations involved.

Washington, D. C.
July 1923.

Note at the time of Proof Inspection

In a more recent paper ("Sitzb.preuss.Akad. May 3, 1923, pp. 110-115), Nernst and Noddack express strong doubt as to the general applicability of thermodynamic treatment of photochemical partial reactions, which doubt is shared by the writer. They nevertheless state that the chain or multicyclical theory probably remains the most likely one for the hydrogen-chlorine reaction. At the same time, they suggest the possibility that it may be the Cl_2 molecule which is activated, and which reacts directly with H_2. The HCl formed retains an excess of energy for a short time which it is able to impart afresh to other Cl_2 molecules. This is the theory originally put forward by Bodenstein (Z.Elektrochem.22,53-61 (1916)), which would have a more general applicability than the atomic chain theory, as was pointed out by the writer ("Chemical Effects of Alpha Particles and Electrons", p. 141). The probability that the energy of activation can be imparted in this way has received indirect but strong support in the recent results of Cario and Franck (Z.Physik. 11, 161-6 (1922)).

Washington, November 1923.

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[1] H. C. P. Weber: Chem. Met. Eng. 27, 94? (1922)

ON THE CATALYTIC HYDROGENATION OF CERTAIN OILS

BY LOUIS KAHLENBERG AND TSU PEI PI

In a previous article[1] on the catalytic hydrogenation of cottonseed oil a number of new catalysts were mentioned and the conditions under which the best results may be obtained with them were described. The present paper is a continuation of that research, the object being to find still other and more effective catalysts and to test these not only on cottonseed oil, but also on soy bean oil, olive oil, corn oil, neat's foot oil, and fish oil, as well as on the free fatty acids actually prepared from each of these oils in the laboratory.

The method of experimentation was exactly the same as that employed before, the hydrogenation being conducted at atmospheric pressure in this case in the apparatus shown in Fig. 3, J. Phys. Chem. 25, 98 (1921). The hydrogen used was ordinary commercial hydrogen obtained in compressed form in steel cylinders. The gas was passed through concentrated caustic potash solution and then through concentrated sulphuric acid before conducting it into the oil to be hydrogenated. The experimental results obtained follow:

Hydrogenation of Cottonseed Oil with Various Catalysts

1. *Nickel oxide catalyst.*

About ten grams of nickel nitrate were decomposed by heating in a porcelain crucible. After the evolution of NO_2 had ceased, the resulting nickel oxide was subjected to reduction by hydrogen at 335° to 340° C for three hours. The reduced substance was then carefully transferred to the tube[2] containing 100 C.C. of cottonseed oil. The hydrogenation was conducted at a temperature of 210° C. After three hours, the oil solidified at room temperature. Its iodine number had been lowered from 109 to 63, and its melting point had become 41° C.

2. *Nickel molybdate catalyst.*

Ten grams of nickel chloride were dissolved in 200 cc of distilled water. To this solution, about eighteen and one-half grams of sodium molybdate dissolved in 200 cc of water were added. The precipitate was washed until free from sodium salt. The nickel molybdate was dried, ground to a fine powder, and finally reduced in a current of hydrogen at 350°-360° C for three hours. The catalyst thus prepared was added to 100 cc of cottonseed oil, without coming into contact with the air. Hydrogenation was then carried on at 240° to 250° C for three hours. After having cooled to room temperature, the oil became a very soft solid. Its iodine value was reduced from 109 to 84, and its melting point was 25° C.

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[1] Kahlenberg and Ritter: J. Phys. Chem. 25, 89-114 (1921)

[2] Fig 3, J. Phys. Chem. 25, 98 (1921)

3. *Nickel tungstate catalyst.*

The method of preparation of the nickel tungstate was practically the same as that of preparing nickel molybdate, sodium tungstate being used in place of sodium molybdate. The nickel tungstate was reduced in hydrogen at 370° C for three hours. After cooling in a hydrogen atmosphere, it was transferred into 100 cc of cottonseed oil. The hydrogenation was carried on at 250° to 260° C. At the end of three hours a sample was taken and it was found that its iodine value had changed from 109 to 82, and its melting point had become 30° C. At the end of four hours, its iodine value was further lowered to 52° and its melting point raised to 42° C.

4. *Tungsten oxide catalyst.*

Pure tungsten trioxide was reduced in a stream of hydrogen at 400° to 420° C for five hours. It changed from yellow to blue in color. About 5 grams of this catalyst was put into 100 cc of cottonseed oil, and the latter was hydrogenated for three hours at 250° to 260° C. On cooling, the oil did not show any tendency to solidify, and its iodine value was nearly the same as that of the original sample.

5. *Nickel silicate catalyst.*

To an aqueous solution containing ten grams of nickel chloride, nine and one-half grams of sodium silicate were added to precipitate nickel silicate. The precipitate was washed with warm water until no trace of sodium salts could be detected in the filtrate. The nickel silicate was dried, ground to a very fine powder and then subjected to hydrogen reduction, in a combustion tube at 250°-290° C for three hours. After cooling, it was introduced into 100 cc of cottonseed oil. This catalyst remained suspended more uniformly in the oil than any other catalyst used in the preceding experiments. The hydrogenation was carried on at 180°-200° C for three hours. The iodine value was changed from 109 to 40 and the melting point was raised to 44° C. The hardened fat was very white and had acquired an odor quite different from that of the original oil.

6. *Nickel borate catalyst.*

Nickel borate was prepared in the same way as nickel silicate except that borax was used as the precipitant. The nickel borate was reduced at 285°-290° C for three hours. The oil was hydrogenated in the presence of this catalyst at 200° C. A sample was taken at the end of three hours and found to have an iodine value of 60. Originally it was 109. The hardened fat melted at 42° C. This catalyst also remained well suspended in the oil.

7. *Iron silicate catalyst.*

An aqueous solution containing ten grams of sodium silicate was treated with a little more than an equivalent amount of ferrous sulphate in solution. The formation of insoluble ferrous silicate took place instantaneously. The precipitate was washed with hot water until it was entirely free from sulphates, which are commonly believed to be "poisonous" to the activity of a nickel catalyst. After drying and pulverizing, the powder was subjected to reduction at 330°-350° C for three hours. This catalyst was introduced into the cottonseed oil without coming into contact with air. After three hours of hydrogenation, the iodine value of the oil was only slightly lowered, namely from 109 to 105.

Ferrous tungstate was prepared and tested in the same manner as the silicate. It was found that there was no change in the iodine value of the oil, even after the hydrogenation had been continued for three hours.

8. *Iron-nickel silicate catalyst.*

To a sodium silicate solution, an equivalent amount of ferrous sulphate and nickel chloride solution was added to precipitate the combined silicates of iron and nickel. This precipitate was thoroughly washed with hot water till free from chlorides and sulphates. It was reduced by hydrogen at a temperature of 300° C for three hours. The reduced substance was added to 100 cc of cottonseed oil, and the hydrogenation was conducted at 180° to 200° C. After three hours, the oil was still in a liquid state at room temperature. The iodine value had changed from 109 to 94. On comparing these results with experiment 5 it is evident that the presence of iron greatly diminishes the catalytic activity of nickel.

9. *Nickel glycinate catalyst.*

Five grams of freshly precipitated and thoroughly washed nickel hydroxide were heated in 150 cc of distilled water with about eight grams of glycine until the liquid became perfectly clear. On cooling, nickel glycinate of a sky blue color gradually crystallized out. After being dried, a portion of it was put directly into the cottonseed oil and hydrogen was run into the mixture for three hours at a temperature of 220°-230° C. There was no appreciable change in the iodine value of the oil as compared with that at the start. Another portion of the nickel glycinate was reduced below 235° C for three hours (because above that temperature it was found to decompose) and the hydrogenation was repeated in the usual way. The result was again negative.

10. *Nickel tyrosinate catalyst.*

Nickel tyrosinate was prepared from the amino-acid tyrosine and nickel hydroxide. It was very difficult to keep it in good suspension in the oil. At the end of three hours of hydrogenation, the oil had neither changed its iodine value nor its melting point.

11. *Thorium stearate catalyst.*

Ten grams of stearic acid were heated with the equivalent amount of potassium hydroxide. To the solution of potassium stearate thus formed 3.2 grams of thorium chloride in solution were added. The insoluble thorium stearate was washed with hot water by decantation and then transferred to the filter and washed. This thorium salt was reduced at 140° to 150° C for three hours. The hydrogenation was conducted in the usual manner at 220° to 240° C. After three hours, the oil seemed to have become somewhat thicker. The original iodine value, 109, was lowered to 101.

12. *Thorium silicate catalyst.*

Thorium silicate was prepared from thorium chloride and sodium silicate, and reduced at 340° to 350° C for three hours. The hydrogenation was conducted for three hours at 220° to 240° C. The oil did not show any sign of solidification even when chilled with ice.

13. *Nickel chromate catalyst.*

To prepare nickel chromate, a sodium chromate solution was treated with nickel chloride. After the precipitate had been thoroughly washed, dried and pulverized, it was subjected to hydrogen reduction in a combustion tube at 320° C. for but two hours. The catalyst thus prepared was carefully transferred into the tube containing 100 cc of cottonseed oil. This catalyst is pyrophoric. It must therefore be kept out of contact with the air. The hydrogenation was performed at 220° C for three hours. The oil solidified to a white fat at room temperature and this fat melted at 41° C. The iodine value had changed from 109 to 62.

14. *Nickel manganate catalyst.*

Nickel manganate was obtained by precipitation using solutions of sodium manganate and nickel chloride. The precipitate was washed with distilled water as soon as it had been formed, because the manganate on standing easily oxidized to permanganate. The nickel manganate was then reduced at the same temperature as in the preceding experiment. After three hours of hydrogenation, the iodine value of the oil was lowered from 109 to 62, and the melting point became 40°.5 C.

15. *Cobalt silicate catalyst.*

The catalyst was made by treating an aqueous solution of sodium silicate with a cobalt chloride solution. For one portion of the precipitated cobalt silicate, the temperature of reduction by hydrogen was not allowed to exceed 350° C. As a result, at the end of three hours' hydrogenation at 180° to 200° C, the cottonseed oil was still found to be a liquid at room temperature. For another portion of cobalt silicate, the temperature of hydroge nreduction was raised to 380°-400° C. With the catalyst thus obtained, the oil solidified on cooling, after having been hydrogenated for the same period of time at 180° to 200° C. The solidified fat melted at 37°.5 C, and had an iodine value of 71.

All of the foregoing results are summed up in Table I.

Hydrogenation of Soy Bean Oil with Various Catalysts

16. *Nickel silicate catalyst.*

From experiment 5, it is evident that nickel silicate forms the best catalyst for the hydrogenation of cottonseed oil. But when nickel silicate, prepared and reduced in exactly the same way as in experiment 5, was introduced into a tube containing 100 cc of soy bean oil having an iodine value of 130, it exhibited only a very slight catalytic activity, the oil being still liquid

Table I

Summary of the results of the hydrogenation of the cottonseed oil, whose original iodine value was 109.

The time of reduction of each catalyst in hydrogen was three hours, except in the case of tungstic oxide, when it was five hours. The time of hydrogenation was always 3 hours, except in the case of nickel tungstate* when it was 4 hours.

Catalyst	Reduction Temp. °C.	Hydrogenation Temp. °C.	Iodine Value after Hydrogenation	Melting Point after Hydrogenation °C.
Nickel oxide	335–340	210	63	41
Nickel molybdate	350–360	240–250	84	25
Nickel tungstate	370	250–260	82	30
* " "	370	250–260	52	42
Tungstic oxide	400–420	250–260	109	liquid
Nickel silicate	290	200	40	44
Nickel borate	290	200	60	42
Iron silicate	330–350	250	105	liquid
Fe-Ni-silicate	300	200	94	"
Nickel glycinate	–	220–230	109	"
" "	235	220–230	109	"
Nickel tyrosinate	–	220–230	109	"
Thorium stearate	140–150	220–240	109	"
Thorium silicate	350	240	109	"
Nickel chromate	320	220	62	41
Nickel manganate	320	220	62	40.5
Cobalt silicate	350	180–200	109	liquid
Cobalt silicate	380–400	180–200	71	37.5

at room temperature after three hours of hydrogenation. The iodine value was reduced only to 112, no matter how long the hydrogenation proceeded.

17. *Nickel borate catalyst.*

Although nickel borate was not as efficient as nickel silicate in the hydrogenation of cottonseed oil, it worked better in the case of soy bean oil. Nickel borate was prepared and reduced in the same manner as before described. The hydrogenation was conducted at 200° C for three hours. Solidification of the oil took place with ease at room temperature. The fat had an iodine value of 78, and a melting point of 33° C. This experiment would indicate that *hydrogenation depends on the specific nature of the oil used, as well as on the individual catalyst.*

18. *Nickel molybdate and nickel tungstate catalysts.*

These two catalysts were prepared in exactly the same way as before. It was found that at the end of three hours of hydrogenation, neither of the two catalysts had worked satisfactorily. By the use of nickel molybdate, the iodine value of the oil was only slightly lowered, namely from 130 to 122. By the use of nickel tungstate, there was no appreciable change in iodine value, even after hydrogenation for six hours.

19. *Nickel chromate catalyst.*

The method of preparation and the time and temperature of reduction of this catalyst were exactly the same as in experiment 13. The hydrogenation was carried on at 220° C. Samples were taken and tested at one hour intervals. The results are given in Table II.

TABLE II

No. of Hrs. of Hydrogenation	Iodine No. before Hydrogenation	Iodine No. after Hydrogenation	Melting point of the product
1	130	105	liquid
2	130	74	33
3	130	63	41
4	130	55	44

The color of the hardened fat was not as white as that of the hardened cottonseed oil.

20. *Nickel manganate catalyst.*

The experiments with nickel manganate were conducted exactly like those with nickel chromate in experiment 19. The results are given in Table III.

TABLE III

No. of Hrs. of Hydrogenation	Iodine No. before Hydrogenation	Iodine No. after Hydrogenation	Melting point of the product
1	130	105	liquid
2	130	72	34
3	130	62	42
4	130	53	45

Attempts were also made to harden soy bean oil by using as catalysts cobalt silicate, iron silicate, nickel formate, nickel oleate, nickel stearate. However, all of these experiments were unsuccessful.

Hydrogenation of Various Oils with Nickel Silicate as Catalyst

The nickel silicate catalyst was used in the following experiments because it had been found the most efficient one in the work on cottonseed oil.

21. *Olive oil.*

Pure California olive oil was preheated at 140° C. for an hour before hydrogenation. The nickel silicate, which was prepared as before, was added to the oil. The hydrogenation was conducted at 220° C. for eight hours. Samples were taken and tested at one hour intervals, and the results are given in Table IV. (The original iodine value of the olive oil was 80).

TABLE IV

No. of Hrs. of Hydrogenation	Iodine value after Hydrogenation	Melting point of the product
1	70	liquid
2	68	30
3	64	32
4	60	33
5	58	34.5
6	52	39
7	52	39
8	52	39

It is evident from Table IV that the hydrogenation of the olive oil reached its maximum at the end of the sixth hour, beyond which time the iodine value and melting point of the oil remained constant. The hardened fat was very white in color.

22. *Corn oil.*

The hydrogenation was conducted at 250° to 255° C. for four hours. A sample was tested hourly. The diminution of the iodine value of the oil stopped at the end of the third hour. The oil did not solidify as a whole, but on standing only a small portion separated out at the bottom of the tube as a white mass. The experimental data are given in Table V.

TABLE V

(The iodine value before hydrogenation was 115)

No. of Hrs. of Hydrogenation	Iodine value after Hydrogenation	Melting point of the product
1	113	liquid
2	101	"
3	95	"
4	95	"

23. *Neat's foot oil.*

The neat's foot oil was a high grade oil obtained from Armour and Company. It was hydrogenated at 220°-230° C. The hydrogenation proceeded very slowly, and ceased at the end of the third hour. The results are given in Table VI.

TABLE VI

(The iodine value of the neat's foot oil before hydrogenation was 77)

No. of Hrs. of Hydrogenation	Iodine value after Hydrogenation	Melting point of the product
1	76	liquid
2	75	"
3	74	"

On account of this rather unusual result, the experiment was repeated. The results obtained were very practically the same.

24. *Fish oil.*

The hardening of fish oil (obtained from fish caught in Lake Michigan) was carried on at 220°-230° C. for six hours. The oil had an unpleasant odor during the process. Samples were tested every hour. The results are given in table VII.

TABLE VII

(The iodine value of the fish oil before hydrogenation was 140)

No. of Hrs. of Hydrogenation	Iodine value after Hydrogenation	Melting point of the product
1	138	liquid
2	133	"
3	124	"
4	110	"
5	109	"
6	109	"

In order to find the limit of conversion of cottonseed oil into hardened fat, and of oleic acid into the corresponding stearic acid by the aid of nickel silicate (which was rather the best catalyst according to the preceding experiments), the oil and the acid were each separately hydrogenated in the following experiments, 25 and 26.

25. *Cottonseed oil.*

The hardening of cottonseed oil was performed exactly as before described. A sample was taken and tested at the end of each hour, until the iodine value of the oil no longer changed. The data are given in Table VIII. The reduction of the iodine value and the rise of the melting point of the oil are also shown by means of the curve in Figure I.

TABLE VIII

(The iodine value of the cottonseed oil before hydrogenation was 121)

No. of Hrs. of Hydrogenation	Iodine value after Hydrogenation	Melting point of the product	No. of Hrs. of Hydrogenation	Iodine value after Hydrogenation	Melting point of the product
1	94	liquid	14	30	52
2	78		15	29	53
3	65	32	16	27	54
4	55	39	17	25	55.5
5	51	40	18	23	57
6	48	41.5	19	21	58
7	45	43	20	19	59
8	41	44	21	17	60
9	38	45	22	14	61
10	35	46	23	12	62
11	33	48.5	24	11	64
12	32	50	25	10.5	65
13	31	51	26	10.5	65

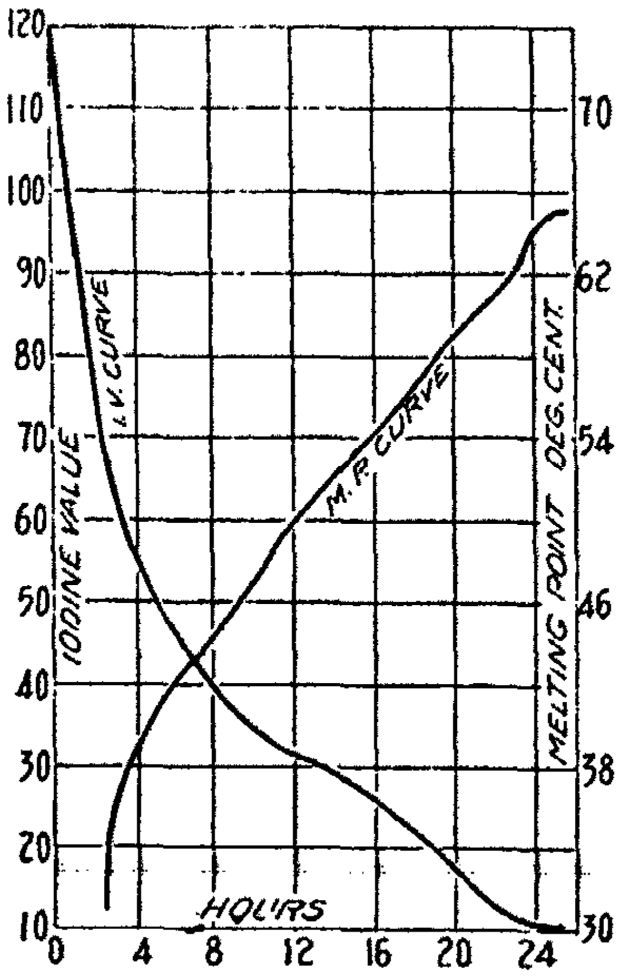

Fig. 1
Hydrogenation of Cotton Seed Oil

26. *Oleic acid.*

The hydrogenation of oleic acid was continued for thirty-two hours, and the reaction came to a stop at the end of the thirty-first hour. This series of experiments indicates that the optimum temperature for the conversion of oleic acid into stearic is 200°-220° C. Above that temperature, the acid became brown in color and developed a disagreeable odor. Table IX gives the results. The changes in the iodine value and melting point of the oleic acid are also presented in the form of curves in Figure 2.

TABLE IX
(The iodine value of the oleic acid before hydrogenation was 90)

No. of Hrs. of Hydrogenation	Iodine value after Hydrogenation	Melting point of the product	No. of Hrs. of Hydrogenation	Iodine value after Hydrogenation	Melting point of the product
1	74	liquid	17	40	43
2	70	"	18	38	44
3	67	"	19	35	45
4	65	23	20	32	47
5	64.5	25	21	30	49
6	62.5	28	22	27	51
7	61	29	23	25	52
8	59.5	31	24	21	54
9	58	32	25	19	56
10	56	33	26	17	59
11	55	33.5	27	16	60
12	54	34.5	28	15	60.5
13	52	35	29	14	61.5
14	50	36	30	13.5	62
15	47	38	31	13	63
16	44	40	32	13	63

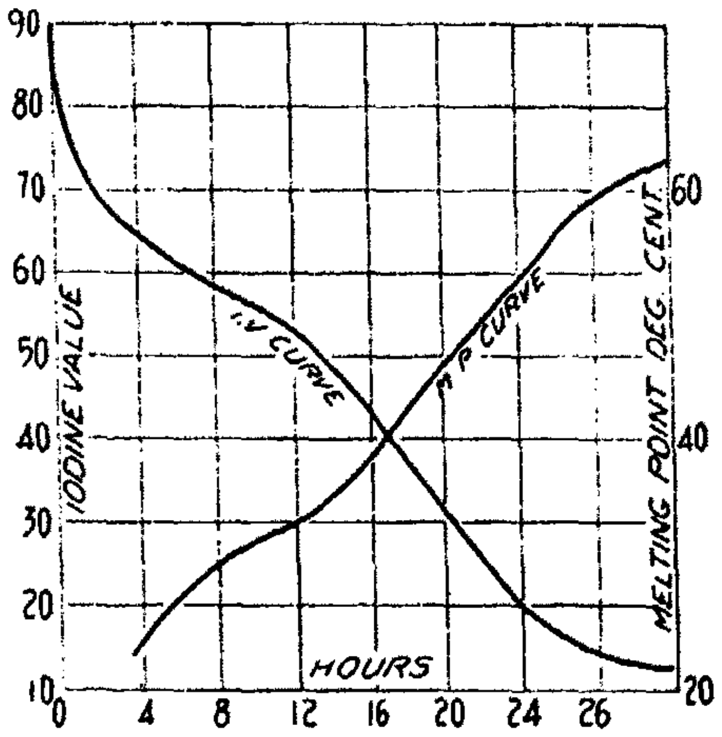

Fig. 2
Hydrogenation of Oleic Acid

To investigate whether it is easier to hydrogenate oils (which are glycerine esters) or the corresponding free fatty acids, the following experiments were performed. Cottonseed oil, soy bean oil, fish oil, and neat's foot oil were hydrogenated as already stated. In experiments 27, 28, 29, and 39, the free fatty acids obtained from these oils respectively, were hydrogenated by means of the best catalyst found, namely, nickel silicate. These free fatty acids were obtained in each case by saponification of the oil in question with alcoholic potash, the soaps being then decomposed with hydrochloric acid, the free acids thoroughly washed with water, and dried before hydrogenation.

27. *Acid from cottonseed oil.*

A hundred grams of cottonseed oil were saponified with alcoholic potash. The soap which was light yellow in color and transparent, was decomposed by warming with hydrochloric acid. The acid thus liberated was thoroughly washed with water until free from alcohol and then separated from the aqueous liquid by means of a separating funnel. The iodine value, solidifying point and melting point of the acid were determined before hydrogenation. The hydrogenation was carried on for three hours at 220° C. The results obtained are given in Table X.

TABLE X

(The free fatty acid melted at 31° C, solidified at 29° C, and had an iodine value of 102 before hydrogenation)

No. of Hrs. of Hydrogenation	Iodine value after Hydrogenation	Melting point of the product
1	86	34
2	72	37
3	59	41

28. *Acid from soy bean oil.*

A hundred grams of soy bean oil were treated in the same way as the cotton seed oil in the preceding experiment. The soap was not perfectly solid and its color was brown. The data in Table XI are the results obtained after four hours of hydrogenation.

TABLE XI

(The free fatty acid melted completely at 23° C, solidified at 21° to 18° C., and had an iodine value of 136 before hydrogenation.)

No. of Hrs. of Hydrogenation	Iodine value after Hydrogenation	Melting point of the product
1	121	26
2	96	32
3	65	35
4	76	38

29. *Acid from fish oil.*

The free fatty acid of the fish oil was prepared similarly and then subjected to hydrogenation at 200°-210° C.

The results are presented in Table XII.

TABLE XII

(The free fatty acid melted at 25° C, solidified at 21° C, and had an iodine value of 130 before hydrogenation)

No. of Hrs. of Hydrogenation	Iodine value after Hydrogenation	Melting point of the product
1	122	27
2	113	29
3	105	32
4	96	35

30. *Acid from neat's foot oil.*

The neat's foot oil gave a pretty, yellow soap when saponified with alcoholic potash. The acid was obtained as in the preceding experiments. It was subjected to hydrogenation at about 200° C. It was found that *the acid was much easier to hydrogenate than its parent oil.* This experiment was carried on for three hours and the final product obtained was perfectly white and hard. The data are given in Table XIII.

TABLE XIII

(The free fatty acid melted at 23° C, solidified at 21° C, and had an iodine value of 77 before hydrogenation).

No. of Hrs. of Hydrogenation	Iodine value after Hydrogenation	Melting point of the product
1	52	39
2	43	47
3	32	54

Conclusion

Among all the various catalysts tested, nickel silicate proved to be the most active in the hydrogenation of cottonseed oil. The optimum temperature for the reduction of this catalyst is from 290° to 300° C., and that for the hydrogenation of the oil is from 180° to 200° C.

Nickel tungstate was found to be efficient in hardening cottonseed oil. The only objection to it is that it requires a rather high temperature for its reduction.

Iron retards the catalytic activity of nickel, when both of these metals are present in the catalyst. It is therefore obvious that the nickel catalyst must be entirely free from iron in order to acquire its maximum activity.

Soy bean oil has hitherto been found to be very hard to hydrogenate. However, by means of nickel chromate and manganate, this oil was duly hydrogenated. Solidification took place at the second hour, when the iodine number fell to about half of its original value.

The hydrogenation of free fatty acids was found to be very much more readily accomplished than that of the corresponding parent oils. The case of neat's foot oil is an especially striking example of this fact.

Chemical Laboratory,
University of Wisconsin,
Madison, August, 1923.

CATALYTIC ACTIVITY

BY C. O. HENKE AND O. W. BROWN

Catalytic Activity and Overpotential

Rideal,[1] from theoretical deductions, arrived at the conclusion that metals with low overpotentials were catalytically active while metals having high overpotentials were catalytically inactive. He states that metals having an overpotential "equal to or exceeding 0.455 volt, should, if used as catalysts in hydrogenation processes, show no activity since the energy necessary for desorption exceeds that necessary for the activation of hydrogen in the gaseous state in the absence of a catalytic material".

Rideal cites the fact that the well known catalysts like nickel, copper, platinum, etc., have low overpotentials. Tin, lead, mercury and zinc however have high potentials and he states that these according to Sabatier, are inactive in hydrogenation processes.

In a previous paper[2] we have given the results of several experiments with tin as catalyst. It was found to be an excellent catalyst for the reduction of nitrobenzene to aniline. Material yields up to 99% aniline were secured. Yet, according to Rideal's calculation, tin should have no catalytic activity or at the most very low activity. Thus Rideal lists tin as having an overvoltage of 0.43 to 0.53 volt. Caspari found the overvoltage to be 0.53 volt.

Lead likewise has a high overpotential and should, according to this idea, be inactive catalytically. Yet we have shown[3] that lead is an excellent catalyst for hydrogenation processes. Not only does lead produce aniline but under some conditions 55% yields of azobenzene were secured. With a suitable catalyst yields of over 96% aniline are obtained. Thus lead does not act as Rideal would predict from its overpotential which he lists as 0.42 to 0.78 volt. The overvoltage as determined by Caspari is 0.64 volt.

According to Rideal's idea both tin and lead should be inactive catalytically or at the most their catalytic activity should be very low. However we have shown that these metals are not only catalytically active but in fact are excellent catalysts. This then would indicate that there is no relation between overpotential or overvoltage and catalytic activity.

Specific Action of Catalysts

The catalytic production of good yields of azobenzene has only been secured with lead, bismuth and thallium[4] as catalysts. The production of azobenzene seems to be specific, at least to quite a large extent. Small amounts of azobenzene were secured with gold, antimony, chromium and manganese. The amount of azobenzene produced by these catalysts was

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[1] J. Am. Chem. Soc., **42**, 94 (1920)

[2] Brown and Henke: J. Phys. Chem. **27**, 739 (1923)

[3] Henke and Brown: J. Phys. Chem. **26**, 324 (1922)

[4] Henke and Brown: J. Phys. Chem. **26**, 324, 636 (1922)

extremely small. Nickel, copper and silver produce no azobenzene. We have used about 33 different copper catalysts, with a wide range of activity, and have carried out nearly 600 experiments with copper as catalyst, yet, we have never secured any solid red azobenzene. Likewise nickel and silver do not give it.

Sabatier[1] states that with copper as catalyst and an insufficient excess of hydrogen the product obtained is colored an orange red by a certain amount of azobenzene or even of untransformed nitrobenzene. A colored product is easily obtained with any catalyst, the color possibly being due to azobenzene but we have never been able to obtain any solid red azobenzene with copper, nickel or silver as catalysts.

Lead, bismuth and thallium on the other hand give azobenzene in quantity. Lead catalysts have been prepared giving as high as 55% yields of azobenzene. Also other lead catalysts (prepared differently) have given over 96% yields of aniline. Bismuth and thallium catalysts have given over 90% yields of azobenzene. With thallium we have never secured as high as 10% yields of aniline. Thus these three catalysts, lead, bismuth, and thallium, give azobenzene and aniline but do not give cyclo compounds. Copper and silver give amines but do not give azo compounds or cyclo compounds. Sabatier[2] states that copper does not attack the aromatic nucleus. Nickel and cobalt give amines and cyclo compounds but do not give azo compounds. This indicates that in the reduction of nitrobenzene these catalysts are quite specific. Their activity and even the product formed may be varied but only within certain limits. Thus lead may be prepared to give aniline or to give in addition to aniline large amounts of azobenzene, but it does not give cyclo compounds. Nickel may be made to give cyclo compounds or to give amines, with but a small amount of cyclo compounds, but it does not give azo compounds. Copper and silver, on the other hand, give only amines and neither azo compounds or cyclo compounds.

Thus catalysts, in the reduction of nitro compounds, seem to be quite specific. On the other hand Adkins and Krause[3] in a study on the decomposition of ethyl acetate by alumina, titania and thoria come to the following conclusion: "Experimental confirmation of the statement that alumina, titania and thoria catalyze specific decompositions of ethyl acetate, has not been obtained. The results obtained by us indicate that in determining the order of efficiency of these catalysts for these reactions, the method of preparation of the catalyst is of equal if not greater importance than the particular metallic element present in the catalyst." Again Adkins[4] in a later paper states: "Alumina has been preferentially activated for decarboxylation and for dehydration by modifying its method of preparation." However it would be interesting to know the highest percentage yield obtainable in each of the three reactions by each of the three catalysts, using each catalyst under the best conditions for that catalyst for each reaction. One catalyst would probably work best at one temperature and another at a different temperature.

[1] Compt. rend., 133, 321 (1901)

[2] "Catalysis in Organic Chemistry," p. 181 (1922)

[3] J. Am. Chem. Soc., 44, 385 (1922)

[4] J. Am. Chem. Soc., 44, 2186 (1922)

Also one catalyst would give the highest percentage yield of reaction 1 (as numbered by Adkins and Krause) under one set of conditions, while an entirely different set of conditions might be required to give the highest percentage yield of reaction 2 and still another set for reaction 3. It might thus be found that one catalyst would give the highest yield of one reaction while another catalyst would give the highest yield of another reaction.

Catalytic Activity and Atomic Weight

In connection with the production of azobenzene it was pointed out in a previous paper[1] that the three catalysts which produce azobenzene, thallium, lead and bismuth, fall together when the elements are arranged according to their atomic weights. Thus thallium has an atomic weight of 204, lead 207 and bismuth 208. No other element has an atomic weight between 204 and 208. No other catalyst has been found to give azobenzene in appreciable amounts. However these three catalysts under suitable conditions give azobenzene in large quantities. Thus there seems to be a relation between atomic weight and the property of producing azobenzene.

Catalytic Activity and Oxidation

In discussing the action of iron and antimony in a previous paper[2], it was pointed out that apparently the metal partially reduced the nitrobenzene and was itself converted to the oxide. Thus at the lower temperatures these catalysts would quickly lose their activity. Their activity however was quickly restored by heating to a higher temperature in hydrogen. This would indicate that at the lower temperature the nitrobenzene oxidizes the metal to the oxide, and hence the catalyst loses its activity. Then at this lower temperature the oxide is not reduced or only slowly reduced by the hydrogen. When the temperature is raised the oxide is reduced and hence the catalyst regains its activity. While at the higher temperatures the catalyst does not lose its activity or at least much more slowly, presumably because at this temperature the oxide is reduced as fast as it is formed.

Summary

1. The fact that tin and lead have high overvoltages and are excellent catalysts while the previously known catalysts, as nickel and platinum, have relatively low overvoltages indicates that there is no relation between catalytic activity and overvoltage.
2. In the reduction of nitrobenzene catalysts are specific. Their activity and even the product obtained may be varied but only within certain limits.
3. There seems to be a relation between atomic weight and the property of acting as a catalyst in the formation of azobenzene.
4. The behavior of iron and antimony catalysts indicates oxidation of the metal by the nitrobenzene and subsequent reduction of the oxide by hydrogen.

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[1] Henke and Brown: J. Phys. Chem., 26, 636 (1922)

[2] Brown and Henke: J. Phys. Chem. 26, 278 (1922)

THE DISCOVERY AND SEPARATION OF THE ISOTOPES OF CHLORINE AND THE WHOLE NUMBER RULE

BY WILLIAM D. HARKINS AND T. H. LIGGETT[1]

1. Introduction

The first discovery of the non-elementary nature of a light "element" was entirely accidental. On January 17, 1913, J. J. Thomson, in an address to the Royal Institution, stated that he had found a second line in the positive ray spectrum of neon, with the explanation given in the following quotation: "There is, however, the possibility that we may be interpreting Mendeleef's law too rigidly, and that in the neighborhood of the atomic weight of neon there may be a group of two or more elements with similar properties, just as in another part of the table we have the group iron, nickel, and cobalt."

The idea that an element whose exact element (so-called atomic) weight differs by more than 0.1 per cent from a whole number, is a mixture of two or more isotopes, was advanced in 1915 by Harkins and Wilson in a series of papers on the "Whole Number Rule".[2] In these papers the atomic weight of the lighter isotope of chlorine was given as 35.00, and it was pointed out that the atomic weights indicated a general difference of 2 between adjacent isotopes. In 1916 Harkins and Turner began an attempt to separate the isotopes of chlorine, a notice of the beginning of this work having been published by Harkins and Hall.[3] Chlorine gas was diffused through the stems of church-warden smoking pipes, and the atomic weights of the residue and diffusate were determined by the gas density method. The first results were inconclusive, so experiments were begun using hydrogen chloride gas. Chlorine had been selected in the first place because it could be obtained in the liquid form in iron cylinders, and because it is easily condensed from the gaseous to the liquid or solid form. However, if there are two isotopes, Cl and *Cl*, of the monatomic substance, there are *three* molecular isotopes[4] Cl-Cl, Cl-*Cl*, and *Cl*-*Cl*. Now the second of these has a molecular weight which is the mean of those of the other two, so it reduces the rapidity of the separation of the atomic isotopes by one-half. This disadvantage is overcome by the use of hydrogen chloride in which each of the atomic isotopes is combined separately with a very light atom.

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[1] Contribution from the Chemical Laboratories of the University of Chicago and of Central College, Pella, Iowa.

[2] These papers contained the first statement of the modern "Whole Number Rule" or the " Law of the Constancy of the Packing Effect." The evidence presented in support of the whole number rule was that contained, (1) in the chemical atomic weights, and (2) the facts then known concerning radioactivity. The facts brought out by the later work on positive rays have given a strong support to the rule but they have in no way modified the form which was given to it by Harkins and Wilson nine years ago. References: Harkins and Wilson: Proc. Nat. Acad. Sciences, **1**, 276 (1915); J. Am. Chem. Soc., 1367-1421 (1915), Phil. Mag., **30**, 723-34 (1915).

[3] J. Am. Chem. Soc., **38**, 221 (1916)

[4] Harkins: Science **51**, 289-91 (1920)

The work of the present paper was begun in 1917, but was stopped by incidents connected with the beginning of the war. An atomic weight determination made in August 1919, indicated that a partial separation of isotopes had been attained, but the atomic weight determinations were made somewhat hastily, so they were not entirely conclusive.

In January 1920 Harkins and Broeker obtained definite evidence, since carefully confirmed, that they had secured five grams of chlorine, with an atomic weight 0.055 units higher than that of ordinary chlorine.[1] Five atomic weight determinations made by an extremely accurate density method gave results as obtained at that time: 0.052, 0.059, 0.057, and 0.053 units increase in atomic weight. The efficiency of the process was 60 per cent; that is about 60 per cent of the theoretical change of atomic weight was actually obtained. The further progress of this separation, which was proceeding rapidly, was stopped about two months later by the illness and death of Mr. Broeker.

The importance of this work lies not only in the fact that it was the first actual separation of an element into isotopes, but in addition it was an entirely independent discovery of the existence of isotopes of chlorine, practically coincident with experimentally, and much earlier theoretically, than that in which the much more rapid positive ray method was used by Aston. A second, and entirely independent separation of the isotopes of chlorine was obtained by Harkins and Hayes.[2] They obtained larger quantities of isotopic material by diffusion through pipes of porous porcelain prepared by the Bureau of Standards. The increase of atomic weight obtained was 0.04 unit, and the efficiency, about 35 per cent, or considerably less than that of the earlier work. This was due to the fact that the pores of these pipes were larger than those of the church-warden pipe stems.

The present paper describes another independent separation in which an increase of 0.043 unit was obtained. Its value is due to its entire agreement with the two separations reported earlier, even though the method used in the determination of the atomic weight is entirely different.

2. Apparatus and Method of Separation

The apparatus used in the present work consisted essentially of a set of 16 church-warden pipe stems connected in series and jacketed by larger tubes similar to condenser jackets. In order to save space a part of the tubes were contained in a gas-tight plate-glass box. A rapid current of dry air was kept passing through the outer jackets and the glass box, but great care was taken to keep the pressure in the jackets and inside the porous tubes as nearly equal as possible. Hydrogen chloride produced by the interaction of concentrated sulphuric and hydrochloric acids was passed at a uniform rate through the inner porous tubes, after which any hydrogen chloride which had not diffused out was absorbed by passing the gas over the surface of water in a series of absorption tubes. The solution constituted the residue or the heavy

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[1] Harkins: Phys. Rev., 15, 74 (1920); Science, 51, 289-91 (1920); Nature, 105, 230-1 (1920).

[2] J. Am. Chem. Soc., 43, 1822 (1921).

fraction. The admixed air which had diffused into the porous tubes, after being thus freed from hydrogen chloride, passed directly into the air of the room. The air from the outer jackets, which contained the diffusate or light fraction, was freed from hydrogen chloride in a separate set of absorption tubes. The apparatus was similar to that used by Harkins and Hayes,[1] which has been fully described.

Three sets of diffusions, each with a cut of approximately 20, were made by the use of this apparatus, so the final cut was approximately 8,000, which corresponds to an increase of atomic weight of about 0.08 unit. Thus the separation actually attained corresponds to an efficiency of about 54 per cent, which is in good agreement with that obtained by Harkins and Broeker by the use of an almost identical apparatus. It may be stated that, in agreement with what may be expected from the standpoint of the theory of the various processes[2] a similar diffusion at low pressures as carried out by Harkins and Mann has given efficiencies of 90 per cent or more.

3. Purification of the Chlorine Compounds

The solution of hydrogen chloride from the first diffusion was given a preliminary purification by distillation in an apparatus of hard glass. The middle fraction alone was used for further purification, but this and the two end fractions were tested for iodine and bromine as described later, but no trace of either of these elements was found. However, to add to the certainty that these elements were absent the middle fraction was redistilled after the addition of a few crystals of potassium permanganate. The middle fraction from this redistillation was used for further treatment. This method of separating bromine and iodine is recommended by Richards.[3]

The hydrogen chloride from the last middle fraction was converted into potassium chloride by the addition of very pure potassium carbonate. This last salt was prepared by recrystallizing 3 times beginning with 5 pounds of the pure salt. This was of the best grade which could be purchased. The potassium chloride thus obtained was still further purified by careful fractional recrystallization. The hydrogen chloride from the further diffusions was purified in the same way.

The final yield of highly purified salt was 16 grams for the diffusions completed in June 1920, and 2.22 g. from the intermediate fraction obtained later. The heaviest chlorine was obtained in July 1921, and was reduced by the extensive purification to 3.08 grams of potassium chloride.

4. Methods of Analysis

Isotopic and ordinary potassium chlorides prepared from the same potassium carbonate and purified in exactly the same way as described above, were used for the determination of the relative atomic weight of the isotopic chlorine.

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[1] J. Am. Chem. Soc., **43**, 1922 (1921)

[2] Harkins and Mulliken: J. Am. Chem. Soc., **44**, 37-65 (1922).

[3] Richards: Carnegie Publication No. 125.

The purest silver used by the U. S. Mint was obtained from them. It was cleaned by washing successively in alcohol, ether, nitric acid, and distilled water. It was then cut into pieces of about 1 gram each and kept in a desiccator.

Precipitation of the Silver Chloride. Three of the 1 g. pieces of silver were weighed carefully and were placed in 400 ccm. beakers, 10 ccm. of 6 N nitric acid, entirely chlorine free, was added, and the silver disssolved by the aid of gentle heating, which also effected the removal of nitrogen dioxide. The silver nitrate thus prepared was diluted to N/10 concentration, and heated to 75°. Slightly less than the equivalent amount of the respective potassium chloride solution, diluted to N/10 concentration, was then dropped in from a pipette, with constant stirring. The beakers were then warmed a few minutes on the hot plate, and allowed to stand until the solution had become clear, which usually occurred in from 4 to 10 hours. Enough potassium chloride was then added with constant stirring, to make very slightly more than the equivalent amount, and the heating and settling again repeated, a *third* slight amount of potassium chloride was added to insure complete precipitation and this was followed by 24 hours standing.

The solutions were filtered through crucibles of the Munroe type with a very thick platinum sponge, burnished on top until it had the appearance of sheet platinum. Over this a perforated platinum disc was used, partly to prevent possible injury to the filtering surface—though it was so hard as to make this unnecessary but chiefly to enable the major part of the silver chloride to be easily removed for fusion. These crucibles proved extremely satisfactory, since they could be used for many determinations with losses in weight in only the fifth decimal place, and often were found to check to within 0.00001 gram.

Filtration and Washing. The crucibles were supported by rubber rings in glass funnels which were placed inside copper funnels, the space between the funnels being filled with finely chopped ice.

The liquid over the precipitate was decanted through the crucible, and the precipitate was then washed 10 times by decantation with ice-cold water containing 5 ccm. of 6 N nitric acid per liter. During this process the beaker was kept, whenever possible in a bath kept at 0°. The transfer of the precipitate to the crucible was made with extreme care to prevent any loss. Finally the sides of the beaker were cleaned by the use of a carefully prepared rubber "policeman," and the completeness of the transfer proved by rinsing the beaker with a few ccm. of ammonium hydroxide and acidifying with nitric acid. The precipitate in the crucible was then washed 10 times with wash water of the same kind until the volume of the wash water had become 175 ccm., the pressure in the suction flask being kept constantly 200 mm. below that of the atmosphere. The precipitate was usually free from soluble chlorides after 100 ccm. of wash water had been used.

The crucibles were wiped on the outside by a clean cloth, and after 10 hours heating in an electric furnace at 250°, they were cooled three hours in a desiccator placed beside the balance, after which they were weighed. After this the heating and cooling were repeated until the weight became constant to 1 or 2 units in the 5th decimal place.

The major portion (90 to 98%) of the precipitate was then removed from the top of the disc by the use of a small spatula, and placed in a quartz crucible which was weighed at once. It was then heated to 250° for some time, cooled, and again weighed. If the weight had changed more than 0.00002 g., the heating was repeated until the weight became constant. The quartz crucible was then set inside a nickel crucible in which it was supported by a ring of metal, and was heated until the silver chloride fused into a single mass. The silver chloride was always pure white before heating, and was slightly darkened by heating, but it finally formed a light-colored, translucent mass. The crucible was rotated so that the silver chloride would not include gas bubbles. After cooling and weighing, the fusion was repeated to make sure that the weight had become constant. The fusion correction averaged 0.00006 g. per gram of silver chloride.

5. Weighing and General Procedure

The Ainsworth balance used for the weighings had a rated sensitiveness of 1/50 mg., but by using 1 mg. riders both for getting the zero point and for the weighings, always taking the zero point just before and just after the weighings, and by using a lens for reading the scale, it was found that there was not more than 1/100 mg. difference between successive weighings of 1 g. of silver. The crucibles were counterpoised by other crucibles of slightly less weight. The weights used were calibrated both at the beginning and the end of the work by the use of 4 pieces which had been standardized under Class M Weights by the Bureau of Standards, with corrections to 0.001 mg. for the 10 and 100 mg. pieces, and 0.01 mg. for the 1 and 10 g. pieces. Each weight which was used was checked against two of the standard weights, with the exception of the smallest and largest, which were checked against one. All determinations were corrected to weight in a vacuum.

In order to minimize the effects of dust, light, vibrations, and change of temperature, all of this work was done in a separate room in which no other work was being done. Daylight was not allowed to act on the precipitates, and the lighting was produced by a red screen over a tungsten bulb. All of the water used was of the "conductivity" grade. The beakers were of hard glass.

The Munroe crucibles were cleaned by washing 5 times with 15N ammonium hydroxide to dissolve almost all of the silver chloride, and by subsequent standing in ammonium hydroxide of the same concentration for 5 hours. They were then washed successively with ammonium hydroxide, water, dilute nitric acid, and finally 10 times with the wash water slightly acidified with this acid. After drying 4 hours at 250° and weighing, this process was repeated until the weight became constant.

6. Determination of Silver Chloride in the Wash Water

Two methods, the nephelometric and a non-nephelometric method, were used for the determination of the silver chloride in the wash water. The latter of these two methods was used at first since at that time no nephelometer was available. It consisted in making extra determinations in which three complete sets of washings were used. In this way it was found that 0.00007 g. of silver chloride was lost in each washing, a value which agreed well with the nephelometric determinations.

The method of using the nephelometer was briefly as follows:

(a) Both vials were first filled with a comparison suspension of infusorial earth, prepared as described below. The right-hand vial was set at 20 mm, and the left hand one adjusted till equal illumination was secured. This was usually at 22 mm. The left-hand vial was then allowed to remain filled with this suspension and set at this height, the right-hand vial being used for both the standard silver chloride suspension and the unknown suspension from the wash water. The left-hand suspension thus served the same purpose as a counterpoise on a balance when weighing by the method of substitution.

(b) The right-hand vial was then filled with the suspension prepared from the wash water as described below, and the reading taken.

(c) Lastly the right-hand vial was filled with a standard suspension of silver chloride prepared in precisely the same manner, and its reading taken. The relation between the unknown suspension and the standard was then easily calculated, or read from a nephelometric curve, drawn as described below.

Fairly accurate results may be secured by assuming that the concentrations are inversely proportional to the readings but it was found more exact to take the readings on a series of suspensions of concentrations ranging from five times that of the standard to one fifth its value; then from these to construct a nephelometric curve, plotting readings against concentrations of silver chloride. The concentration of an unknown silver chloride suspension could then be found as soon as its reading had been determined.

The comparison suspension was prepared by shaking infusorial earth with distilled water, allowing it to stand from 5 to 10 days, and siphoning off the top liquid. This was freed from dissolved air by warming to 40° C, then shaking vigorously in a suction flask under good vacuum for 3 to 5 min. No trouble was then experienced with accumulation of air bubbles in the top of the tube.

The standard silver chloride suspension with which the unknown solutions were compared was made by taking

5 cc	0.0001 Molar	$AgNO_3$
3 cc	1 Molar	HNO_3
3 cc	1 Molar	NaCl

These were mixed and diluted to a definite volume so as to produce a suspension of the same order of concentration as that of the unknown. The precipitate was fully developed by heating to 40° for 30 min. as recommended by

Lamb[1] and his co-workers. It was then re-dissolved with 1 cc 15N NH_4OH, re-precipitated with HNO_3 heated at 40° for 30 min. as before, cooled and the reading taken. Richards[2] has called attention to the necessity of this re-precipitation in order that the precipitates in both unknown and standard may be formed by similar chemical reactions.

All water used in the solutions and suspensions was of conductivity grade, freshly distilled and carefully protected from dust. Tests on some water of the same grade which had been kept in storage bottles for several weeks showed a considerable opalescence. The water for each set of determinations was therefore tested to make sure that its opalescence was negligible.

Since close checks in setting a nephelometer are difficult to obtain, several readings were always taken and the average used.

The results of one series of determinations, with conditions as in the regular analysis, are given below.

Serial No.	Average Reading	Ratio to Standard Suspension 0.25×10^{-6} Molar AgCl	Grams AgCl in 175cc Wash Water
W8 A	28.5	0.898	0.000 056
W8 B	30.0	0.853	0.000 054
W 10	26.4	0.970	0.000 061
W 11	24.6	1.041	0.000 065
W 12	31.9	0.830	0.000 052
W 13	35.4	0.748	0.000 047

These results are in good agreement with the gravimetric method first used, since the difference between the two methods would affect the atomic weight only slightly in the third decimal place.

7. Tests for Bromine and Iodine

Tests for bromine and iodine were made on both the diffusion fractions and the solutions and mother liquors obtained in the various purifications of the chlorides used in this work, but neither element could be detected. For iodine the nitrous acid test and the nitrosyl sulfuric acid test were used. With nitrous acid, especially when starch was used as an indicator, the presence of 1/100 mg. of iodine in 0.8 g. of potassium chloride could easily be detected. The test for nitrosyl-sulfuric acid seemed to be equally sensitive when made upon potassium iodide alone, but for the detection of a small amount of iodine in a large amount of potassium chloride the nitrous acid test was more sensitive.

The best test for bromine which was tried was that with chlorine water and carbon disulfide. The sensitiveness was found to be 1/10 mg. of bromine in 1-g. of potassium chloride. The results of this test were negative in all cases, even when the mother liquors were used.

It should be remembered that although iodine and bromine were thus found to be absent, all of the material used in the atomic weight determinations

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[1] J. Am. Chem. Soc., 42, 251 (1920)

[2] J. Am. Chem. Soc., 29, 623 (1907)

was subjected to several different processes, any one of which would have been sufficient to remove either or both of these elements if they had been present.

8. Atomic Weight of the Isotopic Chlorine

The method used for determining the atomic weight of the isotopic chlorine obtained from the heavy fraction of the diffusions, was essentially a comparison with the atomic weight of ordinary chlorine as assumed with a value of 35.46. An atomic weight of 35.459 corresponded with the purity of the silver used as 99.967%, so this value was used in the tables below.

TABLE 1. Atomic Weight of Isotopic Chlorine

Diffusion	Silver Taken	AgCl Obtained	Ratio Ag : AgCl	Atomic Weight	Average	Cut	Units Increase over Ordinary Chlorine	Total Efficiency
1	1.05896	1.40714	1.328794	35.470	35.471	20	0.012	43%
	0.98209	1.30500	1.328798	35.471				
2	1.08664	1.44409	1.328949	35.487		400	0.029	51%
	0.84085	1.11745	1.328953	35.488	35.488			
3	0.83386	1.10826	1.329072	35.500		8000	0.044	51%
	0.98187	1.30502	1.329117	35.505	35.503			
	(b). Ordinary Chlorine.							
	1.08095	1.43631	1.328748	35.465				
	1.07361	1.42648	1.328676	35.458				
	1.21695	1.61697	1.328707	35.461				
	1.14899	1.52662	1.328663	35.456				
	1.11777	1.48517	1.328690	35.459				
					35.459			

It will be noted that the percentage efficiency of the diffusions was nearly constant, being 51% at the end of both the second and the third diffusions. The apparent lower efficiency of the first diffusion is probably not real, since an atomic weight higher by 0.002 unit would have given its efficiency a value of 50%. The increase in the atomic weight caused by the first diffusion is so small as to make the calculated efficiency extremely sensitive to very slight errors in this case. The theoretical increase in atomic weight is given by the equation of Mulliken and Harkins:

$$M = 0.022 \log_{10} C$$

9. Summary

1. By a cut of 8,000 the atomic weight of chlorine was increased by 0.044 unit. The process used was the diffusion of hydrogen chloride into air through a membrane of porous porcelain. In a process of separation which is 100% efficient the increase of atomic weight should be 0.086 unit, so the efficiency of the actual separation was 51%. This agrees well with the efficiency of 60% obtained by Harkins and Broeker in a separation announced in Febru-

ary 1920, especially since church-warden pipe stems were used as the porous membrane in both cases; and is higher than that of 35% obtained by Harkins and Hayes, who used a material with larger pores.

2. The efficiency obtained in a cut of 400 was also 51%, which is in perfect agreement with that for a cut of 8,000. Such an agreement could not be attained unless the process described had actually separated the isotopes, since the material separated after each diffusion was purified before the next diffusion was begun, so impurities could not have such a constant effect.

3. The atomic weights were determined by the method of precipitation of the chlorine as silver chloride, and are in good agreement with those obtained in independent separations by Harkins and Broeker and Harkins and Hayes, who used a density method for the atomic weight determinations.

4. The experimental work here reported was begun in 1917 in order to give support to the "Whole Number Rule" of Harkins and Wilson. The element chlorine was chosen because its atomic weight differs more from a whole number than that of any light element, so it was considered that a considerable amount of the heavier isotope would be present mixed with the isotope of atomic weight 35.0.

Chicago, Ill.,
Sept. 21, 1923.

NEW BOOKS

The Chemistry of Leather Manufacture. *By John Arthur Wilson. 23×16 cm; pp. 343. New York: The Chemical Catalog Co., 1923. Price: $5.00.*—"Raw skin is readily putrescible in the wet state. Upon drying, the collagen fibers become glued together and the skin becomes very stiff. Although the dried skin will not putrefy, it again becomes putrescible as soon as it comes into contact with water. Thousands of years ago the discovery was made that the properties of skin substance change completely when the wet skin is brought into contact with the aqueous extract of those forms of plant life which have since come to be classed as vegetable tanning materials. The action which brings about this change of properties is known as vegetable tanning and the compound of skin protein and tannin as leather. Under normal conditions, the fibers of leather do not glue together upon drying and they are not putrescible even in the wet state. . . . Two conditions may be accepted as essential to successful tanning: the first that the natural physical structure of the skin shall be changed but very little; the second that the degree of tannage shall be as nearly uniform as possible throughout the skin. The second condition, in a large measure, is essential to the first," p. 240.

"It has often been supposed that the tanning action consists of a coating of the skin fibers with tannin; but observations of sections under the microscope indicate that this is not the case. The outer surfaces of the skin act as filters, permitting only the soluble matter to pass into the interior, where it subsequently diffuses into the substance of the fibers, which assume a uniform color throughout when tanning is finally complete. In finished leather, contrary to what seems to be the general belief, we find no coating of the surfaces of the fibers nor any material precipitated in the spaces between them," p. 256.

"The simplest theory of chrome tanning is that it consists of the combination of chromium and collagen, forming a series of salts that might be called collagenates of chromium. From this chemical theory, there are theories of many shades and kinds all the way down to the assumption that chrome tanning consists of a precipitation of colloidal chromic oxide upon the surfaces of the skin fibers.

"In following chrome tanning by means of the microscope, the author has observed the chrome liquor diffuse into the skin and also into the substance of each fiber, but without any visible sign of precipitation. When tanning was complete, each fiber looked like a transparent rod of green glass. This is similar to the phenomenon observed in vegetable tanning.

"Thompson and Atkin recently attempted to apply the Procter-Wilson theory of vegetable tanning to chrome tanning. The electrical charge on the collagen may be accepted as positive during chrome tanning and it seemed improbable to Thompson and Atkin that combination takes place between positively charged collagen and a positively charged chromium ion or complex. In a review of eighty papers dealing with chromium salts, they found numerous contradictions on points of importance, but one fact seemed to stand out as definitely established. Chromic sulfate exists in solution in two modifications, one green, the other violet. At any temperature between 0° and 100° C, a definite equilibrium exists between the two forms in solution, the green being more stable at high and the violet modification at lower temperatures. In the change from violet to green by raising the temperature, equilibrium is quickly reached, but in the reverse actiom, following a lowering of the temperature, equilibrium is reached only after a long time. Thompson and Atkin offered the theory that chrome tanning is effected by an anion or negatively charged colloidal particle containing chromium and arising from the green modification of chromic sulfate. The action should then be similar to that described in the Procter-Wilson theory of vegetable tanning," p. 305.

"The author's view of the mechanism of chrome tanning is as follows: Although the degree of ionization of the carboxyl groups of the protein, in which a hydrogen ion passes into solution, may become extremely small with increasing acidity, it never becomes zero. This means that, even if the electrical charge on the protein structure is predominantly positive there still remain a relatively small number of negatively charged groups scattered throughout this structure. $Cr(OH)_2^+$, or ions of a similar nature, diffuses into the jelly composing the fibers of the skin and combines with these negatively charged groups wherever encountered. Having centralized the electrical charges on each other, both the collagen and chromium groups become capable of ionizing further, the chromium group giving off another hydroxide group and the collagen a hydrogen ion. With a repetition of this process, all three bonds of the chromium become united directly with the collagen structure. The fundamental assumption underlying this view is that however small may be the concentration of negatively charged groups in the collagen structure under the conditions of tanning, it is very much larger than would result from the dissociation of the chromium compound of collagen.

"This theory is not antagonistic to the Proctor-Wilson theory of vegetable tanning, but actually supplements it. In vegetable tanning, the tannin probably attaches itself to the amino or other basic groups of the protein structure; in chrome tanning, the chromium attaches itself to the carboxyl or other acid groups. This is corroborated by the fact that chrome tanning apparently does not lessen the capacity of the skin for combination with vegetable tanning materials, or vice versa. Wood found that plates of gelatin tanned with chromium were capable of combining with as much tannin as before the chrome tanning, suggesting that the chromium and tannin are not attached to the same groups in the protein structure. This is not in accord with the Thompson-Atkin theory, in which both chromium and tannin would be attached only to the positively charged groups of the protein. That the collagen undergoes a chemical change in chrome tanning is proved by the fact that it loses its property of being convertible into gelatin by contact with boiling water." p. 308.

"Ever since chrome tanning was first introduced, the relative merits of chrome and vegetable tanned leathers have formed the subject-matter for debate. Too often, however, the attempt was made to compare a poor grade of one kind of leather with a good grade of the other, without taking into consideration differences in the original skins and in the methods of manufacture of the leathers. Since the resistance of a leather to tearing, for example, is a function of the grease content, the moisture content, and the extent to which the thickness of the original skin has been reduced by splitting, any comparison between two kinds of leather must take all of these factors into consideration. There are, however, certain differences between chrome and vegetable tanned leathers that are incontrovertible and more or less independent of the details of manufacture. These only will be considered in making the comparison," p. 30c.

Photographs are given of vertical sections of vegetable and chrome tanned leathers made from the same skin. After bating, the skin was cut into halves along the line of the back bone. One half was tanned with chrome liquor and the other with vegetable tanning materials. When finished, each leather represented an excellent specimen of shoe upper leather of its particular kind.

"The outstanding difference in appearance is the much larger size of the fibers of the vegetable tanned leather. In the chrome tanned leather, the fibers are thin, as in dried, raw skin, but in the vegetable tanned leather, the fibers have grown to such an extent that they almost completely fill the interfibrillary spaces. But this difference in size of the fibers is only what one would expect from the fact that 100 grams of skin protein combined with 57.0 grams of tannin, in the case of the vegetable tanned leather, as against only 7.2 grams of chromic oxide, in the other. This difference is responsible for the greater weight and solidity of vegetable tanned leather. Either leather can be made tough and as soft as desired by the introduction of a sufficient amount of oil, but the vegetable leather is capable of absorbing a much greater quantity of oil without becoming raggy. By comparison with the vegetable leather, the chrome leather feels empty.

"Another outstanding difference between the two kinds of leather is the relatively high sulfuric acid content of the chrome tanned leather compared to the negligible amount present in the vegetable leather. This particular sample of leather showed by analysis 6.65

grams of sulfuric acid per 100 grams of skin protein, which is typical of leathers of this type on the market. It should be recognized, however, that this sulfuric acid is not entirely free, but is combined either with the chromium compounds or with the skin protein. Only a trace of acid is free at any time, but as soon as this trace is removed by washing with water, more is immediately liberated by hydrolysis.

"Attempts to free chrome leather from sulfuric or other mineral acid, without damaging the leather in some way, have not been successful, so far as the author is aware. Reducing the content of sulfuric acid much below that normally occurring in chrome leather seems to cause brittleness, although the cause of this is not known. In making comparative tests, the author has always found shoes made from vegetable much more comfortable, especially on long walks, than shoes from chrome leather and has attributed at least part of this difference to the hydrolyzable sulfate present in the chrome leather.

"The rise of chrome tanning has been favored by its speed and comparative simplicity. The manufacture of vegetable leathers requires a much longer time and more labor. In the manufacture of light leathers, not sold by weight, tanners have naturally preferred to switch to the quicker method of tanning with chromium salts, although some of the best grades of upper leather are still tanned with vegetable tanning materials. In the manufacture of heavy leathers, sold by weight, tanners have been forced to adhere to the older method of vegetable tanning in order to get profitable yields. Incidentally, the author believes that they also get better leather," p. 300.

Chrome tanning can be reversed by the action of Rochelle salt (potassium sodium tartrate). "The fact that Rochelle salt will dissolve precipitates of chromic hydroxide led Procter and Wilson to suspect that it might have the power to decompose chrome leather. They soaked a piece of fully tanned leather in a normal solution of Rochelle salt over night and found, next day, that it would not stand the boiling test. But after washing and soaking in fresh chrome liquor, containing no Rochelle salt it soon became tanned again. It was found that chrome leather can be detannized by Rochelle salt solution and then again in fresh chrome liquor repeatedly, showing that chrome tanning is a reversible action, under certain conditions.

"The extent to which chrome leather can be freed from chromium by Rochelle salt was shown by soaking a piece of chrome leather in a normal solution of Rochelle salt for two weeks. The solution was colored a deep green and the skin, after thorough washing, was found to be practically free from chromium and resembled a piece of bated skin. Upon heating with pure water, it was gradually converted into gelatin and the solution set to a firm jelly upon cooling. This work has since found application in preparing chrome leather wastes for manufacture into glue and for the stripping of the chrome from the surface of leather to be retanned with vegetable tanning materials," p. 297.

Two of the processes preceding the actual tanning are unhairing and bating. "What is probably the oldest method known for unhairing skins received the name sweating from the nature of the process in its more highly developed state. It consists of little more than the putrefaction of the cells of the Malpighian layer. Since it is only necessary to allow a fresh skin to remain for a day or two in a warm, damp place to cause a loosening of the hair, the method was probably discovered very early in the history of the human race. It is not improbable that the accidental discovery of this action first revealed to the ancients the advantages of unhaired skins for certain purposes.

"Because of the danger of serious damage to the skins in the sweat chambers, unless the process was very carefully watched and controlled, it ceased to be popular for the best grades of skins after safer methods of unhairing were devised. It is still in use in some tanneries for the lower grades of skins, such as the cheaper classes of dried hides and sheep skins where the wool is valued more highly than the skin," p. 151.

"The commonest method in use today for effecting the separation of the epidermal system from the true skin is also one of ancient origin and is known as liming from the fact that saturated lime water is used. Formerly a lime liquor was prepared simply by filling a vat with water and adding calcium hydroxide greatly in excess of saturation. The skins, after soaking, were put into this liquor and allowed to remain there until the hair and epidermis had become so loosened that they could be rubbed off with very little pressure. Often the skins were removed each day and fresh lime added in order to hasten the action. But with a fresh lime liquor it usually required weeks for the skins to get into a state where the hair would slip easily. It was discovered that less time was required for each succeeding lot of skins passing through a given liquor. The longer a liquor was used the more it became charged with ammonia, other protein decomposition products, bacteria, and enzymes, all of which assisted in loosening the hair. The older liquors, however, attacked the collagen fibers to a greater extent and also produced less swelling of the skin proteins than fresh liquors," p. 156.

"It was suggested by the author that barium and calcium hydroxides hydrolyze proteins to a lesser extent than the hydroxides of sodium or ammonium because of the higher valency of the cations. The swelling of proteins in alkaline solution is due to the pull of the cations of the protein salt, which tend to diffuse from the region of high concentration of ions in the jelly to the region of lower concentration in the surrounding solution. If this pull is sufficiently great, we might reasonably expect a breaking up of the units making up the protein jelly. A sodium or ammonium ion exerts its entire pull upon a single unit, whereas the pull of a divalent cation is divided between two units, making the tendency towards decomposing the protein only half as great. This valency effect, however, is not the only one playing a part in sterile unhairing liquors because the mere replacement of half of the hydroxide ions of lime water by sulphate ions is sufficient to cause a very marked increase in the rate of unhairing. Wood and Law suggested that Schlichte's observation of the unhairing power of sterile lime water is further complicated by the formation of sulfur compounds by the action of lime on the easily dissolved sulfur of the hair. Such compounds are capable of loosening the hair," p. 163.

"Apparently anything that will hydrolyze the newly formed cells of the epidermis without injuring the rest of the skin is a satisfactory unhairing agent. Lime owes its popularity to the safety attending its use. Its limited solubility makes it possible to maintain a constant hydroxide ion concentration at about 0.03 mole per liter simply by using an excess. This concentration is high enough to retard putrefaction considerably and yet not great enough to injure the skin itself, since the solute is a diacid base. It is entirely possible, however, that the popularity of lime will wane when some of the newer methods of unhairing reach a higher stage of development," p. 172.

"Perhaps the most curious of all the processes involved in making leather is that of bating. Little is known of its origin because it was a secret process, but it is at least some centuries old. After the skins are taken from the lime liquors, unhaired, scudded, and washed they still contain lime in the form of carbonate and in combination with the skin proteins. At this stage they are plump and rubbery and tanners have experienced many difficulties due to putting the stock directly into certain types of vegetable tan liquors when it was in this condition. The object of bating is to prepare the unhaired skins for tanning and originally consisted in keeping them in a warm infusion of the dung of dogs or fowls until all plumpness had disappeared and the skins had become so soft as to retain the impression of thumb and finger when pinched and sufficiently porous to permit the passage of air under pressure. When hen or pigeon manure was used, the process was called bating, and when dog dung was used it was called puering, but the term bating is now applied to the process generally, regardless of the materials used. The difference in terminology naturally disappeared with the advent of artificial materials," p. 173.

"After examining hundreds of sections of skin taken before and after bating, at high magnifications and with the employment of a great variety of stains, Wilson and Daub came to the conclusion that the removal of elastin is the primary function of bating and that the other actions associated with dung bates can all be produced by the simple chemical control of the processes other than bating. The falling of the skin, however, always accompanies the removal of elastin because the range of pH values over which pancreatin acts upon elastin is such as to reduce the plumping of limed skin to the point accepted as a measure of the completion of the bating process," p. 185.

The subject is treated under the general headings: introduction; histology of skin; chemical constituents of skin; ionization of acids and bases commonly used in the tannery; physical chemistry of the proteins; preservation and disinfection of skin; soaking and fleshing; unhairing and scudding; bating; bleaching and pickling; the tannins; vegetable tanning; chrome tanning; other methods of tanning; finishing and miscellaneous operations.

In addition to the passages quoted, the reviewer is much interested in the author's method of estimating tannin, p. 224; in the partial conversion of nontannins into tannins during concentration, p. 228; in the effect of pH in determining the fixation of tannin, p. 276; in the action of neutral salts on the rate of tanning, p. 266; in the effect of neutral salts on chrome tanning, p. 293; in alum, iron, silicic acid, and oil tanning, pp. 311, 313, 315, 317.

In a casual way one is glad to learn that dandruff "is not the result of a disease; but is rather evidence that the epidermal cells are functioning and reproducing vigorously," p. 25; also that when the pigment-containing cells in the skins are collected in spots they appear as freckles, p. 27; and that "when a hair is shed, after reaching the limit of its existence, the epithelial cells left surrounding the hair papilla keep on multiplying, and soon another hair is formed to replace the one shed. Baldness results from the failure of the blood vessels of the papilla to furnish the required nourishment or from the destruction of the epithelial cells in some other way. Any serious attempt to grow hair on a bald head must be accompanied by some means of introducing living epithelial cells into the hair follicles, of which there are something like a thousand to the square inch. In other words, we cannot grow a crop without seedlings," p. 31.

"Attached to each hair follicle, just below the sebaceous glands, and extending obliquely upward through the derma, almost to the surface, is a bundle of nonstriated muscle tissue, known as the erector pili muscle. The nerves supplying these muscles are known as the pilomotor nerves. These muscles contract under the influence of emotions, such as fear, surprise, anger, or other disagreeable states, or in response to cold or grazing tactile stimuli. Among the commoner visible effects are the roughening of the skin called goose-flesh and the effect of the hair standing on end, very pronounced in a frightened cat.

"The real purpose of the erector pili muscles is apparently to protect the body against sudden changes of temperature by their control over the operation of the glands; they seem to act as effectively as a thermo-couple in a good thermostat. Their contraction puts a pressure on the glands which causes the cells to give up their oil to the hair follicle and, in the process, the cells are destroyed. The oil is then forced up through the follicle to the surface of the skin, where it tends to stop the action of the sudoriferous glands and the evaporation of water from the surface of the skin," p. 31.

The fifth chapter, on the physical chemistry of the proteins, is undoubtedly the one on which the author prides himself the most and it is certainly the one with which the reviewer has the least sympathy. One wonders at the naive way in which the author postulates, p. 99, that the prediction of results by means of a formula is a proof of the accuracy of the assumptions on which the formula is based, especially since he admits, p. 127, that one deduces the same formula if one has a substance in true solution and a membrane through which one of the ions does not pass, or selective adsorption of one ion at a surface. He admits also, p. 131, that an adsorption formula represents the data for hydrogen ion concentration with gelatine nearly as well as his own formula; but he concludes, p. 132, that "adsorption, so far as it pertains to gelatin jellies, is a manifestation of chemical combination complicated by the separation of the solution into two phases. We see no reason for looking upon adsorption by other materials in any different light. In the case of suspensoids, we are dealing with two phases of the solution apparently analogous to those of gelatin systems, the film of solution enveloping the particles corresponding to the solution absorbed by the jelly."

Evidently the author believes that we get carbon with acetic acid of crystallization when acetic acid is adsorbed by charcoal. On p. 127 he says that "when gold is dispersed in water, the presence of chloride, bromide, iodide, hydroxide ion in concentrations ranging from 0.00005 to 0.005 normal has a marked stabilizing effect on the sol produced, and the particles are negatively charged. The effect seems to be due to the ability of these ions to form stable compounds with the gold. Fluoride, nitrate, sulfate, and chlorate ions decrease the stability of gold sols, which is significant in view of the fact that they do not form stable compounds with gold."

"According to the Procter-Wilson theory of swelling, when a block of gelatin jelly is immersed in a solution of hydrochloric acid, the solution passes into the jelly filling up the interstices. Of the ionized gelatin chloride, which then forms, the chloride ions remain in the solution in the interstices, while their corresponding gelatin cations form part of the net work and are not in solution in the same sense as the anions. In tending to diffuse into the outer solution, the anions exert a pull upon the cations forming part of the network, causing an increase in volume of the jelly proportional to the pull exerted, so long as the elastic limit is not exceeded," p. 118.

"On p. 108 we read that "in alkaline solution the protein ion is negatively charged, while it is positively charged in acid solution. In a solution, originally alkaline, in which the hydrogen-ion concentration is gradually increased, there must be some point at which the protein becomes electrically neutral; that is, where it has an equivalent number of positive and negative charges. The hydrogen-ion concentration at which this occurs has been called by Hardy the isoelectric point of the protein. The isoelectric point of gelatin was found by Michaelis and Grineff to lie at a pH value of 4.7 and this value has been repeatedly confirmed by others."

On p. 111, we find two isoelectric points for gelatin, one at 4.7 or thereabouts and the other at 7.7. If we are to take the definition of an isoelectric point just given gelatine should become positively charged beyond pH = 7.7; but that is too absurd. The author gets round the difficulty by postulating, p. 114, that there is a sol and a gel form of gelatine and that 4.7 is "the isoelectric point of the gel form. The appearance of a second point of minimum swelling at pH = 7.7 seems to indicate that between 4.7 and 7.7 the gelatin passes from the gel to the sol form and that the second point of minimum occurs at the isoelectric point of the sol form."

Of course one cannot expect much of any definition; but it is a very poor one that will not last a page or two. If the sol and gel forms have any influence each on the other, as one would reasonably expect them to have, then neither 4.7 nor 7.7 is a true isoelectric point; but each is merely a compromise point at which the mutual effects of the positive gel and the negative sol or of the positive gel and the positive sol produce a minimum of some sort. It is hard to make heads or tails out of anything so confused as this. Regardless whether the author is right or wrong, he should at least think his fundamental proposition through clearly.

The photographs are marvellous and must have been a labor of love to the author. It seems almost unkind to suggest that the work of his hands is more clear than that of his head. It is also unfair to do so, because the book is an extremely valuable and important one even though we jettison the defective theory.

Wilder D. Bancroft

Gelatin in Photography. *By S. E. Sheppard. Vol. I. 22×15 cm; pp. 263. New York: D. Van Nostrand Company, 1923. Price: $2.20.*—This is the first of two volumes on gelatine and the less interesting one because chiefly introductory. The four chapters are entitled: a history of the applications of gelatin in photography; the manufacture, technochemistry, and general properties of gelatin; physical testing of gelatin.

"Gelatin is generally regarded as consisting of glutin and 'chondrin', of which the latter has recently been found to be a mixture of glutin and chondromucoid. Glutin is the comparatively pure gelatin; chondrin is the main constituent of glue and poor grades of gelatin. A gelatin which can be considered as mainly glutin may be obtained from the corium (the sensitive and vascular layer just beneath the epidermis), while chondrin in a relatively distinct form is a product of the hydrolytic treatment of various cartilages," p. 25.

"In drying gelatin an apparent paradox exists in that the more concentrated a solution, the longer it takes to dry; and conversely, the weaker a solution, the quicker the process. The explanation of this is as follows: a slice of four percent gelatin weighing 75 grams will weigh, when dried, about three grams—that is, 72 grams of water must be removed in drying. The first fifty grams of water are readily taken up by the air current; but after this the surface of the gelatin sheet hardens to an extent which makes it much more difficult to remove the remaining twenty-two parts.

"Since the more concentrated the solution, the sooner surface hardening or impermeability will occur, the final stages of evaporation in the concentrated sol are much slower. Practically, the dilution at which drying can be effected is limited by the difficulty of spreading and netting the weaker jellies, and by the available space," p. 29.

"A considerable difference of opinion has existed as to the solubility of hair and epidermis in lime liquors. Among industrial chemists, solubility is generally accepted. On the other hand, biochemists find that keratin is not soluble in less than twenty per cent caustic alkali in the cold. It has been suggested by Seymour Jones that reconciliation of these opposing results lies in the existence of bacteria and digestive ferments in the unhairing baths. His analysis of the action is briefly as follows: While digestive ferments have great difficulty in rendering adult (dying) keratin soluble, young keratin is readily dissolved by pepsin. The Malpighian layer is built up of young keratin cells and it was observed on many occasions that the lime solutions appeared to attack the lower layer (rete malpighi) first, thus loosening the upper layer in large sheets. On the other hand, Griffiths contends that unhairing is a purely chemical process, not involving bacterial agency. This view, however, is opposed to the balance of the evidence," p. 62.

"It may be emphasized here that little is definitely known as to how far the 'stripping' in lime should be allowed to proceed to secure respectively: culinary gelatins, photographic gelatins, technical gelatins, and glues. Up to the present, adjustment of this has been largely a matter of rule of thumb. Valuable or invaluable as this may be, it appears very probable that it should be supplemented by chemical research and control," p. 69.

"Apart from physical and colloid-chemical characteristics (to be considered later), there are certain special requirements for photographic gelatins. They should give clear and nearly neutral solutions; the moisture content should not be above twenty percent, and lower for 'soft' gelatins; and the ash should not exceed two percent. . . . Bases and heavy metals should not be present in more than mere traces, as they are harmful to photographic emulsions. Sulphates and chlorides should also be low," p. 117.

"Collagens, especially the fibrous type, swell greatly in dilute hydrochloric acid, but shrink in concentrated acid. They also swell in quite weak alkali solutions. They are decomposed in the cold by four or five percent solutions of caustic alkali with evolution of ammonia, but ten percent alkali carbonate solutions at 40°C, cause neither swelling nor decomposition. Heating in weak acid or alkali destroys the gelatin-yielding complex, but concentrated neutral solutions do not affect collagens at 40°C.

"It would follow from this that collagen is a name for a group of bodies having similar properties, but varying considerably, even in composition. Since gelatin and glutin are derived from collagen by treatment with boiling water, there should exist as many gelatins as parent collagens. Gelatinization of the collagen may be accelerated by acids, especially sulphurous acid, by heating under pressure in the presence of alkalies, or by concentrated ammonia solution," p. 134.

"The osmotic properties of gelatin solutions will be referred to in greater detail later (Volume II). Their variability and the indeterminateness of molecular weights of colloids as deduced therefrom has been especially treated by Moore, who suggests that the range of 'solution aggregates' indicated by these vapor pressure and osmotic pressure results points to a physical rather than a chemical complexity of the protein molecule.

"The possibility of the determination of significant molecular weights of proteins by osmotic pressure, etc., methods, may be regarded as revived by the important work of Sörensen on the crystallization and isolation of egg-albumin. Although this will be considered more fully under the physical chemistry section (Volume II), certain conclusions are of great importance in the present discussion. Sörensen's general contention is that emulsoid colloids such as gelatin, albumin, etc., are better defined by differences in degree of reactivity of the dispersoid (dissolved) phase with its dispergent (solvent) than by dispersity (mechanical subdivision). Hence emulsoid solutions resemble true solutions in their behavior, which follows the Phase Rule when the number of the components is rightly chosen. The successful outcome with egg-albumin is no doubt due largely to the possibility of purification by recrystallization as it is nearly ash-free, and free from certain less determinate congeners (mucin, con-albumin).

"On the other hand, the exact determination of the conditions of crystallization with this colloid can probably be extended to other proteins. An important result with regard to osmotic pressure is the following. An egg-albumin solution of a given composition has a constant well-defined osmotic pressure, the magnitude of which is dependent upon the egg-albumin concentration, the ammonium sulphate concentration, and the hydrogen-ion concentration, according to definite laws. The osmotic pressure of an emulsoid solution thus definitely defined is as definite a quantity as that of a crystalloid solution of definite composition.

"These conclusions are not necessarily incompatible with the solution-aggregate hypothesis. The definite osmotic pressure, in the foregoing, would correspond to a definite solution-aggregate, but the magnitude of this aggregate would be determined by definite chemical (valency) forces, rather than indefinite physical forces—such as those implied by the vague concepts capillarity, internal pressure, etc. Again, crystallization is not necessarily the expression of chemical individuality. If the electrostatic neutralization of charged ions can form a regular space lattice, a crystal will be formed, but need not correspond to chemical molecular integration. This question will be taken up again in discussing the physical chemistry of the gel condition, as also will be the theses of Pauli, Procter, and Loeb in regard to the stoichiometric nature of gelatin reactions with acids, bases, and salts, and their dependence upon hydrogen-ion concentration. Provisionally, the most probable 'combining weight' of gelatin may be taken as 840, while the 'molecular weight' is uncertain," p. 148.

While the text is written for the most part in a rather unexpectedly simple and clear manner, there are places, pp. 184, 187, where the reviewer fails to grasp much more than the single words. The author discusses, p. 184, the " general cycle, carrying the simple molecular constituents of the earth's atmosphere and soil through the stages of relatively free elements and complexly united proteins, and back to the simple molecular stage. . . .

"The essential link is photochemical synthesis, to which it may be suspected all biochemical (enzyme) reactions can be reduced in principle,—i.e., actual reactions, to distinguish from ordinary thermochemical reactions which should be properly termed black radiation reactions (Perrin). The other aspect is the occurrence of the synthesis by colloids in colloids, and persisting in colloids. Now, just as laboratory organic chemistry has not, for excellent reasons, accomplished its synthesis from the biocentric standpoint, by biochemical methods, so laboratory colloid synthesis has, for the most part, drifted from a chemical to a mechanical conception of colloids. In particular, the chemist has, with reason, regarded them as interfering with the progress of chemical reactions, while in vital synthesis the maintenance of colloid condition is both the means and the end. Hence, just as Cross and Bevan complain that organic chemists see nothing more in cellulose, etc. (biocolloids), than a polyanhydride of glucose, in proteins than a polyanhydride of amino-acids, so colloid chemists are coming to regard no colloids as more than mechanical sub-divisions of phase.

"These purely chemical and purely mechanical approximations are no doubt of much use, and correspondingly true. There is, however, a gap which is of the greatest importance in the case of biocolloids. That is, how, in biocolloid synthesis and catalysis, is the essential coördination of chemical condensation and mechanical dispersion regulated and maintained?"

That is a little hard reading; but the climax is reached in the criticism of the organic chemical view of protein, p. 187. "All in all, it appears that in a purely arbitrary judgment which has decreed that the basis for color and selective absorption of light of organic compounds should be sought for in characteristic groups, (chromogens, chromophores and auxochromes) and constitutional arrangements of atoms—in structural chemical bases,—while the grounds for colligation (tenacity) and selective adsorption (adhesion) of matter in other organic compounds should not be sought for in characteristic groups (collogens, collophores and auxocolls), but brushed aside as purely physical or mechanical in origin. Actually, they are measured, no doubt, as physical or mechanical quantities,—as jelly strength (tenacity, etc.) and surface tension. But precisely the same is true of color and selective absorption.

"Now, inversely as modifications of the static chemical theories of color by considerations of physical electronic theories and dynamic isomerism are being forced on the chemist, so modifications of the physical or mechanical theories of cohesion and capillarity are being injected by chemists into the haphazard domain of molecular physics.

"This new departure, remarkable because experimentally founded and quantitatively expressed, gives aid to the view that in the colloidal condition there is not only mechanical subdivision but at the same time enhancement of the residual affinities of every atom and potential atom group, and it is precisely this far-reaching and deep-seated dissolution of molecular bondage which allows both the physico-chemical activity and the structural chemical inertia of colloids. The true antithesis is not between crystalloids and colloids, which are indeed continuous, but between crystals and organisms, and the cycle which an atom can undergo could or should be represented in its main features by a closed hysteresis cycle, in which crystallization would be equivalent to disorganization. Actually, laboratory colloids and biocolloids tend continually, through all changes to increase of entropy (reduction of motivity) and crystallization, or, at least, segregation of definite chemical compounds and physical phases. This has been inverted to the point of considering colloids as essentially dispersed systems of ultramicroscopic droplets or crystalloids. Yet this extreme view is not entirely incompatible with the counter-theory just discussed, for it is expressly argued by the supporters of the dispersion theory that "the surface layer of crystals consists of relatively uncoördinated molecules and atoms with greater free energy." Now, as the crystal diminishes to ultramicroscopic dimensions, its surface increases relatively to its volume, so that for the postulated super-ultramicroscopic crystals of emulsoid colloids this 'true crystalline' part would be an approximately negligible amount—particularly *in vivo*, though tending to increase *in vitro*."

Wilder D. Bancroft

A Dictionary of Applied Physics. *Edited by Sir Richard Glazebrook. Vol. I. 23×17 cm; pp. ix+1067. New York and London: The Macmillan Co., 1922. Price: $15.00 per volume.* In the preface the editor says: "During the past twenty-five years the applications of Physics to Industry have grown enormously. The National Physical Laboratory was opened in 1900, while Universities and Technical Colleges have multiplied, and recent years have seen the growth of the Department of Scientific and Industrial Research, with its Research Associations in many fields, its studentships, and its skilled Research workers. Meanwhile, the results of the labours of the past are, for the most part, scattered in the Proceedings of learned Societies or stored in the brains of the active workers to whose efforts they are due.

"To find out what are the latest methods of Calorimetry, what exactly is known about the laws of Friction, how far has the theory of the Steam Engine advanced, what are the principles on which methods of accurate gauging or of the determination of the many factors which come into the lay-out of a big electrical plant, the design of a Dynamo, or the methods of Pyrometry are based, means a long search in Libraries and, not infrequently, a futile journey to some place where it is hoped the wished-for information may be found.

"The Science of Aeronautics, the Design of Optical Instruments, the Methods of Metallurgy, the Construction of Clocks, Telescopes or Microscopes, the Laws of Music and Acoustics are all based on Physics.

"The manufacturer who is concerned with these and, indeed, with countless other subjects must know, not perhaps all that has been done—that would be too heavy a task—but where he may find the latest and most accurate information on the subject with which he is mainly concerned. This it has been the object of the Dictionary of Applied Physics to give. Applied Physics is a wide subject and the task has been a heavy one.

"The Dictionary will appear in five volumes of 800-1000 pages each, and, as will be seen from the names of some of the principal contributors, the Editor has been fortunate in securing the help of those most competent to write on each subject. His thanks are due, in the first place, to those colleagues, without whose cordial help the Dictionary could not have been produced. He is also indebted to a number of Scientific Societies whose Councils have allowed use of illustrations from their Proceedings to be freely made. Among these should be mentioned in particular the Royal Society, the Institution of Mechanical Engineers, and the Institution of Electrical Engineers. The same help has been readily afforded by a number of Publishers.

"It is clear, that, with so large a range of subjects, any individual worker will, probably, be concerned mainly with one branch, and, with this in view, the volumes have been arranged, as far as possible, in subjects. To obtain information as to the latest advances of Applied Electricity it will not be necessary to purchase the sections of the Dictionary dealing with Aeronautics or Meteorology. The arrangement in each volume is alphabetical, but, at the same time, it has been thought best to deal with each main subject—for example, the Thermodynamics of the Steam Engine—in a continuous article; references are given, each in its own alphabetical position, to the headings of the various sections of an article and to the more important subjects which it includes."

The first of the proposed five volumes deals with mechanics and engineering and with heat. Among the more important articles are: air-pumps; calorimetry; the principles of dynamic similarity; elastic constants; engines; friction; heat; hydraulics; lubrication; units of measurement; phase rule; pyrometry; refrigeration; resistance thermometers; steam engine; temperature; thermodynamics; thermometry; steam turbine.

The chemical methods of producing high vacua "have been little practised since the discovery of the powerful absorption for gas of charcoal at low temperatures. From the discovery of the method by Dewar to the invention of the molecular pump in 1913, it was the standard method of producing extreme vacua unattainable by liquid piston pumps. A glass or, preferably, silica tube containing a few grams of charcoal is attached to the vessel to be evacuated. The charcoal is heated during the preliminary exhaustion of the vessel, which should be carried to 0.001 mm.; the vessel is then disconnected from the pump and the charcoal tube cooled in liquid air. If the vessel is large and the highest vacuum is required, two or more charcoal tubes may be attached, one being sealed off before the next is cooled," p. 23.

"But the most practically important process of evacuation dependent on the discharge is that which involves the introduction of phosphorus vapour into the evacuated vessel. It appears to have been discovered first by Malignani; it was applied to the evacuation of electric incandescent lamps and has been used for the same purpose continuously since its discovery. At first it appears to have been thought that the action was chemical, but it is now known to be dependent on the passage of a discharge through the mixture of gas and containing phosphorus vapour.

"The exact conditions which determine the disappearance of the gas are still obscure, but it may be stated generally that if a discharge is passed through any mixture of gas or vapours containing phosphorus vapour the pressure will be reduced more rapidly and to a lower limit than it would be if the phosphorus vapour were absent. The gas that has disappeared can be restored by heating the walls of the vessel to a temperature at which red phosphorus will evaporate. The latest theory of the action is that the gas is deposited on the walls and covered with a 'varnish' of red phosphorus produced by the action of the discharge from the phosphorus vapour, which prevents the re-evolution of the gas so long as the 'varnish' remains; it is also supposed that the exceptional electrical properties of the phosphorus vapour are of importance. It is known that sulphur, iodine, and arsenic act in somewhat the same way as phosphorus in this matter," p. 24.

"The general theory of flash-point determination depends on the hypothesis that flashing takes place when the space above the oil contains a definite percentage of oil vapour mixed with air. This condition will be reached for a definite temperature of the oil surface from which evaporation is taking place, and it is generally assumed that it is this temperature which is given by the thermometer and is the temperature taken as the flash-point. The rate of evaporation, however, depends upon the temperature of the surface of the oil, and investigation showed that this temperature differed appreciably from the thermometer reading throughout the course of a determination. Furthermore, the temperature at different points throughout the oil varied by several degrees at any one moment. The temperature distribution depended in part on the form and dimensions of the apparatus and on the relative amounts of heat reaching the oil from different sources. . . .

"Investigation of the three types of apparatus, namely, the Abel, and the Colonial and the German types of Abel-Pensky apparatus, showed that the temperature distribution in each varied, so that for any definite reading of the thermometer the temperature of the surface of the oil was different in each of the three apparatus. It was further found that the temperature of the surface of the oil at the moment when flashing took place was the same in each of the three apparatus although the thermometer readings differed; the difference in flash-point recorded in the three types of apparatus is therefore completely explained by the consideration of the temperature distribution in the oil cups.

"The general results of the investigation showed that the Colonial type of Abel-Pensky apparatus gave a flash-point 1° F. higher than the original form of Abel apparatus, while the German type of Abel-Pensky gave results approximately 4° F. higher; further, these differences are sensibly constant over the range 70°-100° F. Incidentally there is a systematic difference amounting to about 0.5° F. (taking the mean values for a large series of observations) between apparatus of the same type but fitted with oil and gas test flames respectively. As might be expected from the previous remarks, the gas test flame gives the lower flash-point the flame supplying more heat to the surface of the oil, when adjusted to the specified size," p. 336.

"The fact that the layer of lubricant manifests static friction proves that it behaves under tangential stress like an elastic solid. If it be a fluid when in the mass the effect of the attractions of the solid faces, combined with the traction, must therefore be to confer on a thin layer both orientation of its molecules with respect to the normal, and also solidity. The orientation of the molecules spoken of above is due to the fact that the attraction of the molecules of the solid faces is not the same for all parts of a molecule of the lubricant. We may suppose, for instance, that the attraction for the -COOH or -OH group is greater than for the remainder of a carbon chain. The orientation of the molecules of the lubricant will therefore be greatest at the solid faces and least midway between them, because it tends continuously to be upset and give way to the random relations of the interior of a fluid. The layer of lubricant, therefore, even if it be only two molecules thick, varies rapidly in structure along the normal and the peculiar feature of boundary friction is that the stresses occur in a medium which is excessively heterogeneous along one axis, namely the normal to the solid faces, and homogeneous along the tangential planes," p. 578.

Bismuth "is highly crystalline and so brittle that a plate a few millimetres thick can be broken like a biscuit. It is readily polished, and in the process of polishing an amorphous layer is formed covering the crystal facets which previously were easily visible to the naked eye. This amorphous layer—which may be called the Beilby layer—is formed, as Beilby showed, by a flowing of the metal, and, like a truly fluid surface, it forms under the influence of surface tension. No polishing powder is needed to polish bismuth—the operation can be performed by rubbing the metal on the skin of the ball of the thumb. The skin then becomes covered thickly with a fine dust of metal, a considerable amount of material being rapidly removed from the surface, and the dust is seen under the microscope to be composed of spheres each 0.01 mm. in diameter. The formation of these spheres can be followed under the microscope. At the edge of the plate the flowing surface of the metal is detached in a thin sheet which breaks up into drops under the influence of its own tension. The structure of the dust and its mode of formation are therefore complete evidence of the fluidity of the surface produced by rubbing," p. 578.

"In the early part of the year 1914 an attempt was made to arrive at international agreement as to the adoption of a standard or fundamental temperature scale by the three national standardising laboratories—viz. the National Physical Laboratory, the Bureau of Standards, Washington, and the Reichsanstalt. The outbreak of war prevented formal acceptance of the Centigrade Thermodynamic Scale as the 'international' scale of temperature. This scale has been adopted in the meantime at the National Physical Laboratory.

"Lord Kelvin showed long ago the theoretical advantages of the thermodynamic (or absolute) scale, and also that a perfect gas (i.e. one which obeys Boyle's law and suffers no temperature change when subjected to free expansion with no external work) would give a scale identical with the thermodynamic. The practical advantage of the thermodynamic scale is that the high-temperature scale evaluated on the basis of the laws of radiation is consistent with that of the gas-thermometer at lower temperatures.

"To promote the general use of the same temperature scale in both scientific and industrial circles, the following alternative methods have been agreed to as a means of attaining a 'Practical Scale' of temperature which approximates to the thermodynamic scale. A statement of the exact relationship between the two scales is deferred until a sufficient degree of concordance has been reached in the measurements. There is, however, every reason to believe that the Practical Scale over the range 0° C. to 100° C. agrees within the limits of experimental error with the hydrogen scale of the International Bureau of Weights and Measures," p. 835.

"The steam turbine is an engine or 'prime mover' working on the same principle as the familiar country-side windmill. Instead of a current of air being utilised to rotate a shaft by means of 'sails', a current or blast of steam issuing from a number of fixed nozzles is employed to rotate a shaft by means of 'vanes', 'buckets', or 'blades'.

"In the case of windmills the relatively small power obtainable from air, with a reasonable sail area, and the discontinuity of the breeze, render this type of prime mover of relatively little economic importance. With the steam turbine, however, the case is very different. Not only is there the convenience of uniform rotary motion produced by a steady torque applied to a shaft direct (in common with the windmill), but also the unfailing steam blast generated with coal or oil fired boilers, and the enormous output obtainable from a turbine of very moderate dimensions.

"The economic value, therefore, of the steam-driven rotary engine, or steam turbine, has been the incentive to its development to the utmost, and its evolution has been successfully carried out during the last thirty years in the face of all obstacles, mainly owing to the efforts of Sir Charles Parsons and his associates, until to-day it is by far the largest and mos economical prime mover yet devised. Its efficiency is unrivalled by any other form o steam engine. Units of 30,000 to 40,000 horse-power are becoming commonplace in large land power stations for the generation of electricity, whilst marine installations reach 150,000 shaft horse-power in one vessel," p. 1027.

Wilder D. Bancroft

Some Microchemical Tests for Alkaloids. *Part I. By Charles H. Stephenson. Part II, Chemical Tests of the Alkaloids used. By C. E. Parker. 23×16 cm; pp. 110+28. Philadelphia: J. B. Lippincott Co., 1921. Price: $4.00.*—Over sixty years have now passed since the first pioneer suggested that the microscope could be advantageously employed for the identification of the plant alkaloids by taking advantage of the characteristic appearances of the free bases and of their salts when caused to separate in crystalline forms upon object slides. It was then shown that the secret of success would lie in discovering the optimum conditions and so controlling them as to enable the analyst to work under repeatable conditions.

The practicability of this method of qualitative analysis was most effectively demonstrated by Wormley in his classical work—The Microchemistry of Poisons. The microscopic identification of plant alkaloids had been employed long before Wormley's researches but had attracted little if any interest among chemists; to Wormley must be accorded the credit, therefore, of calling the attention of analysts to the wonderful possibilities of the art of microscopic organic chemical analysis.

No further efforts were made to gather together in book form, the existing data until Behrens issued his treatise on the microchemical analysis of organic substances. In the course of the discussions in this work he described reactions for thirty alkaloids. Kley's enlarged revision of Behrens' work (which now includes 50 alkaloids) must be regarded as the most thorough, trustworthy, and comprehensive guide we have for the identification of the alkaloids by means of the microscope.

Stephenson's little book, devoted exclusively to the alkaloids, consists essentially of an enumeration of the chemical reagents which he has found will cause the separation of crystalline compounds when added to solutions of different alkaloids under the uniform conditions of concentration adopted by him. The book can be justly described as an enumeration only, for the statements contain little information other than the bare fact that a certain reagent added to a neutral solution of a given alkaloid (or salt of an alkaloid) does or does not yield a crystalline compound upon an object slide. Occasionally the author states whether these crystals polarize but no information is given as to the character of the polarization or data as to the more easily determined optical constants of the crystalline bodies.

A still more remarkable omission is the absence of all chemical facts. The reader is told nothing in regard to the chemical nature of the alkaloids discussed nor is there a single suggestion as to the probable composition of the crystals which have been caused to form. From the viewpoint of the analytical chemist this is a most serious omission since, unless he has information relative to the nature of the reaction taking place and as to the probable composition of the product serving as the identification compound, a test is of little value when applied to substances of unknown composition. This is especially true when a test depends entirely upon the appearance of crystals under the microscope.

Following a short introduction the author gives a bibliography of eighteen titles of the more important papers and books which have been published dealing with the microscopic reactions for alkaloids. It would have greatly aided chemists if the several excellent works on botanical micro-technique (as, for example, Tunmann-Pflanzen-mikrochemie) had been included since they all contain much valuable information as to the identification of the plant bases in the cells and tissues.

The author next describes the method of procedure that was adopted, the results of which are enumerated in the book. The reviewer believes that few chemists will be willing to adopt identical concentrations of substances to be tested and the same strength of reagent with each individual alkaloid. Most of us believe that the best results are obtained by varying the equilibrium condition in the test drops. The method adopted by the author consists of adding directly to a neutral solution of the base to be tested (or its approximately neutral solution in dilute hydrochloric acid, if the free base is insoluble) a drop of the solution of the reagent. Concentrations of the alkaloids varying between 1 to 1000 and 1 to 50 were employed but in each individual test the reagent strength remains the same no matter what base was being tested for. Such a system insures uniformity of procedure, but is scarcely good chemistry since no account is taken of the character or of the relative solubility of the compound whose separation is desired. In order that a test may be wholly reliable and that it may be properly interpreted by the analyst it would appear to be essential that he shall be in possession of the nature of the solid phase he wishes to produce and also of the equilibrium conditions under which this phase may be expected to separate in a form sufficiently characteristic to assure its recognition. For these reasons the older method of Behrens of allowing one drop to flow into another through a narrow channel is to be preferred.

The alkaloids are listed in alphabetical order, merely. Under each reagent giving a crystalline deposit, a very brief statement is made of the general appearance of the crystals and whether they are characteristic or not. Three alkaloids—colchicine, solanine, and apocodeine, failed to yield crystalline compounds with all the reagents tried. The results obtained with thirteen other alkaloids have not been recorded in the book because the author considered them of doubtful purity.

The results which were obtained have been arranged in tabular form as an insert at the end of the microscopic part of the book. This table is most interesting and will prove invaluable to all who have occasion to undertake the identification of alkaloids of unknown nature after they have been obtained in a condition of approximate purity by any one of our standard separation methods. The data here gathered together will also prove a time and labor saver to the investigator who may be tempted to enter this intricate, but amazingly fascinating, field.

The tests described are supplemented and rendered more easily interpreted by excellent illustrations consisting of 27 plates comprising 162 photo-micrographs. These plates are beautifully executed and represent an unlimited patience, good judgment and a high degree of technical skill.

The second part of the book, pp. 84-105, is devoted to a critical study of the chemical reactions of the alkaloids used by Stephenson. The author of this section, C. E. Parker, of the Bureau of Chemistry, carefully describes the chemical behaviour of the alkaloids and points out their similarity. The usual standard color, odor and precipitation tests are given for each alkaloid as also the source of the alkaloid (with the exception of eight); a most valuable feature, for, although it is a well known fact that certain alkaloids purchased from different manufacturers may show marked variations in their chemical reactions, few authors state the source of the material upon which they have worked and the reader referring to the literature not infrequently finds it difficult to reconcile the apparent discrepancies in the descriptions given.

Part II would have been rendered more useful for reference had the same typography been followed as appears in Part I. A solid running page with no double spacing between topics and no change in type, combined with the absence of an index forces the reader to glance over page after page in order to locate a particular alkaloid whose chemical reactions he wishes to check.

The expert will find this book of interest and value, particularly as a guide for the development of methods for the examination of impure or complex mixtures.

E. M. Chamot

Errata

In the paper by Dhar and Sen (27, 376), seven lines from top, change $23\mathrm{x}10^{-1}$ to $23\mathrm{x}10^{-5}$.

In the paper by Sharp and Gortner (27, 771), Figures 1 and 2 have wrong legends. Figures 1a, 1b, and 1c are graphic representations of the data obtained with flour from which the salts had been *extracted* with water. Figures 2a, 2b and 2c are similar data obtained on the *unextracted* flours. Whenever Fig. 1 occurs in the text, it should read Fig. 2 and whenever Fig. 2 occurs, it should read Fig. 1.

A REVIEW OF THE CRITICAL CONSTANTS OF VARIOUS GASES[1]

BY S. F. PICKERING[2]

In the following review of the literature on the critical constants of gases an attempt has been made to include all of the available data on the more common gases and, as far as possible, to select what appear to be the best values.

In each case the reasons for choosing particular values are stated. These reasons are necessarily more or less general and future researches may indicate that the values selected are not the best.

It is thought, however, that some such selection should be made because the average reader does not usually have the time or facilities for examining the different papers himself, and the figures given in even the modern physical and chemical tables are often obsolete. Those who are especially interested in the subject can use the references for making their own selections. The selected results are for convenience assembled in a table at the end of the paper.

Only the more recent determinations have been critically considered because it is thought that the methods of purifying the gases and of making the measurements employed by the earlier observers were not sufficiently developed to justify their comparison with the more modern methods. These determinations involve many experimental difficulties and the technique of making them has been materially improved in recent years.

That the methods and apparatus have not been perfected even yet is indicated by the fact that in a number of cases, that of acetylene for example, the results obtained by recent contemporary observers do not agree. Because of these considerations it is often impossible to select values with certainty, and when this is the case the uncertainty is indicated in the table by question marks.

In selecting the best values considerable weight is given to the reputation of the observers, such as Onnes and his co-workers, who have made a special study of this subject. The laboratories at the University of Leyden are perhaps better equipped than any other with both the apparatus and the experienced personnel necessary for making those determinations which involve low temperatures. Cardoso has also published a large amount of careful work on this subject.

The critical temperature of a substance may be defined as the minimum temperature above which the substance can not be liquefied no matter how great the pressure. In this review the value adopted for the absolute zero on the Centigrade scale is $-273.1°$, this being the value used by most of the ob-

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[1] Published by permission of the Director of the Bureau of Standards of the Department of Commerce.

[2] Associate Chemist, Bureau of Standards.

servers. Recent work seems to indicate $-273.2°$ as the more probable value, but it is thought best to retain the former figure to avoid confusion in quoting the results of the various investigators until the newer value is more firmly established.

If the temperature of a substance is increased towards its critical temperature the density of the liquid phase becomes gradually lower and that of the saturated vapor phase becomes gradually higher. Near the critical temperature the meniscus separating the two phases begins to flatten and finally disappears when the critical temperature is reached. At this temperature the physical properties of the two phases become identical and all distinction between gas and liquid disappears. The pressure corresponding to the saturated vapor pressure at the critical temperature is called the critical pressure and the density of the substance at this critical point is called the critical density.

There are two general methods used for the determination of the critical temperature of a substance. One method consists in sealing the substance in a small glass tube (the tube in which the critical phenomena are observed is often referred to as a laboratory tube) and very gradually raising the temperature until the meniscus disappears, after which the temperature is then slowly lowered until the meniscus appears again, the critical temperature being taken as the mean. Care must be taken that the right amount of substance is in the tube in order that the phenomena can be observed; that is, just below the critical temperature there must be present both liquid and vapor phases occupying preferably equal volumes. This method is not particularly accurate, especially if the substance contains small amounts of impurities which retard the establishment of equilibrium.

For further discussion of the appearance of the meniscus and the retardation caused by impurities, the reader is referred to a paper by Kuenen[1] This method has the further disadvantage that it does not permit of measuring the critical pressure.

With the other method the laboratory tube is connected to a suitable manometer and means are provided for varying the pressure. It is very desirable to provide an agitator, in order to insure equilibrium of the sample. The critical temperature is usually taken as that temperature at which a very slight decrease in pressure causes the meniscus to temporarily appear until the temperature of the substance reestablishes itself. This method is used by most of the observers, although in some instances the critical point is determined in a somewhat different manner. For example, Onnes determined the critical constants of neon and of hydrogen by making a series of pressure measurements at constant temperature, the range of these measurements including the range wherein condensation occurs. The volumes of liquid condensed are also determined. A series of such isothermals is obtained starting with temperatures slightly below the critical temperature. From these data

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[1] Kuenen: Comm. Leyden No. 8.

the critical temperature and pressure are calculated. Cardoso[2] in the case of gases other than the so-called permanent gases uses the disappearance of the critical opalescence as a criterion of the critical temperature.

The critical opalescence according to Cardoso and others is caused by the formation, at temperatures slightly below the critical temperature, of a sort of emulsion of the vapor and liquid phases which have approximately the same density. These minute drops of liquid disappear at the critical temperature. According to an alternative explanation, the critical opalescence arises from the unequal distribution of molecules occurring at the critical temperature.

At this temperature the velocities of the molecules vary widely, and at different points even slightly above the critical temperature there might be momentary associations of slowly moving molecules. Because of their slower motions, the temperatures of these momentary minute aggregates would be slightly lower and while they would immediately be dispersed others would form and thus give an opalescent appearance to the substance. According to this explanation the opalescence could appear at temperatures above the critical, in which case most of Cardoso's values for the critical temperatures of the more easily liquefied gases are slightly high.

This question has been discussed quite extensively by various authors[1] but has not been definitely settled as yet.

Because of the extreme compressibility of substances near their critical points, it is very difficult to determine the critical density accurately. In fact the density of a substance at its critical point is not uniform because the pressure varies at different levels. The weight of the substance itself gives rise to a slightly greater pressure at the lower end of the container. Grey[2] states that in a tube 10 cm in height containing pure carbon dioxide at its critical point there may be a difference of 6 per cent between the densities at top and bottom.

The method for measuring critical densities devised by Cailletet and Mathias[3] probably yields the most accurate results. According to this method a series of observations of the densities of the liquid and vapor phases is made at different temperatures below the critical temperature and extending nearly to it.

These determinations of densities when plotted graphically against the temperature give a curve resembling a parabola. If one then plots a series of

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[1] J. chim. phys., 10, 491 (1910).

[2] Einstein: Ann. Physik, 17, 549 (1905)
Travers and Usher: Proc. Roy. Soc. 78, 247 (1906)
Young: "Stoichiometry", 172 (1908)
Onnes and Keesom: Comm. Leyden No. 104
Young: Phil. Mag., Nov. (1910)
Smoluchowski: Bull. Ac. des Sci. de Cracovie, Dec., 1907; Ann. Physik, 25, 205 (1908); Trans. Roy. Soc. (London). 212A, 165, (1912)
Rothmund: Z. physik Chem., 26, 433 (1898); 63, 54 (1908)
Ostwald: Ann. Physik, 4, 35 (1912)
Küster: "Lehrbuch der physikalische Chemie," (1907)

[3] Compt. rend., 115, 720 (1892)

[4] Compt. rend., 102, 1202 (1886)

points representing the means of the densities of the two phases at the same temperatures, a straight line is obtained for most gases. This line is called the rectilinear diameter of the substance and if the equation of the line in terms of the temperature is obtained, the critical density is given by substituting in this equation the value for the critical temperature, for at this temperature the densities of the two phases become equal to each other and to the mean density. The rectilinear diameter therefore intersects the critical temperature ordinate at the point designating the critical density. For some gases, particularly those having a very high critical temperature, the rectilinear diameter has a slight curvature near the critical temperature, but in most cases it may be considered a straight line.

There are several methods for determining the densities of the liquid and saturated vapor phases, but their descriptions are rather lengthy and involved and so can not be properly included in this paper. These methods have been employed with some differences in detail by Mathias,[1] Amagat,[2] and Young and Thomas,[3] and good descriptions of the methods and of the critical phenomena in general are to be found in Young's "Stoichiometry".[4]

Acetylene

Date	T_c abs.	P_c atm.	d_c	Obs.
1879	310.15	68.0	0.36	1
1880	310*			2
1884	310.10*	68.0*	(0.32)	3
1897	308.35	61.02		4
1907	309.6	61.6	0.314	5
1909	310.15		0.2306	6
1910	308.6	61.5		7
1912	308.5±.1	61.65±.1		8
Selected values	309 ?	61.6	0.231	

1. Ansdell: Proc. Roy. Soc. (London) **29**, 209 (1879); Chem. News, **41**, 75 (1880)
2. Dewar: Proc. Roy. Soc. (London) **30**, 543 (1880)
3. Dewar: Phil. Mag., **18**, 210 (1884)
4. Kuenen: Phil. Mag., **44**, 174 (1897)
5. McIntosh: J. Phys. Chem., **11**, 306 (1907)
6. Mathias: Compt. rend., **148**, 1102 (1909)
7. Cardoso and Baumé: Compt. rend., **151**, 141 (1910)
8. Cardoso and Baumé: J. chim. phys., **10**, 509 (1912)

Note: The asterisks placed after some of the values indicate that the particular author did not state how the value was obtained. The parentheses indicate that the enclosed figures were calculated from other physical properties.

For the critical data of substances not herein mentioned the reader is referred to the various tables of physical and chemical constants, such as those

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[1] Ann. de Toulouse, **1891**.

[2] Compt. rend., **114**, 1093 (1893)

[3] J. Chem. Soc., **63**, 1199 (1893)

[4] Young: "Stoichiometry", pp. 160-181, (1908).

of Landolt and Börnstein. Van Laar[1] has published a table containing the critical constants of a great many substances including a large number of organic compounds. The values are selected from different tables and from the results of certain investigators. When one considers, however, the disagreement between observers regarding the critical constants of the more common and more easily prepared substances, it becomes apparent that the data in the above mentioned tables are only approximate, coming as they do in many cases from the work of single observers.

The determinations of the critical pressure of acetylene are quite concordant but those of the critical temperature differ markedly.

All of the observers mentioned below prepared acetylene from calcium carbide and water. McIntosh purified the gas by washing with sodium hydroxide and with chromic acid after which the gas was dried with concentrated sulphuric acid and phosphorus pentoxide and then solidified. As the manometer was calibrated to 40 atmospheres only, there is some doubt as to the accuracy of the value for the critical pressure. The acetylene was not agitated while the observations were being made.

Mathias after removing phosphine and stibine from the acetylene, dried the gas over calcium chloride, passed it through several bulbed tubes maintained at −79° and then solidified it by means of liquid air. The two laboratory tubes in which the critical phenomena were observed were rinsed out with fresh portions of acetylene seventeen times, and evacuated after each rinsing. The whole apparatus including the tubes of solidified acetylene, was then evacuated to a fraction of a millimeter, after which five portions of the acetylene were evaporated and removed by evacuation. The gas was finally vaporized into the laboratory tubes and used for the experiments.

Mathias used Young's method for making his determinations but gives no details.

Cardoso and Baumé bubbled acetylene through potassium permanganate and potassium hydroxide solutions and dried it with phosphorus pentoxide. The gas was then fractionated eight or ten times and introduced into the laboratory tube, which had been previously exhausted by a mercury pump.

Kuenen's sample contained traces of impurity while those of McIntosh and of Cardoso and Baumé were quite pure, as indicated by the fact that the pressure remained practically constant when the gas was condensed at constant temperature.

It seems best, in consideration of the differences between the results of the different observers, to take 309° as the critical temperature.

The critical pressure may be taken to be 61.6 atmospheres.

The method which McIntosh used to determine the critical volume consisted in introducing the gas into a tube provided with a sealed capillary at the top and noting the volume at the critical point. Some of the capillary was drawn off by means of a blow-pipe and the volume determined again. In this

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[1] Proc. Acad. Sci. Amsterdam, 18 II, 1224 (1916)

way several tubes were prepared which were almost exactly filled at the critical point. These tubes containing the acetylene were weighed and the critical densities calculated. The mean of the values so obtained was 0.314. This method, however, is inaccurate because of the great compressibility of the gas at its critical temperature and is inferior to the method used by Mathias as stated in the general discussion of the determination of the critical density.

By substituting 310.5°, his own value for the critical temperature, in the equation for the rectilinear diameter of acetylene Mathias obtained 0.2306 for the critical density. If, instead, 309° is used the critical density becomes 0.2313.

Air

Date	T_c	P_c	d_c	Obs.
1884	133	39		1
1885	about 132.6	37–37.5		2
1896	132.1	39		3
1917	132.37 (a 132.47 (b	37.25 (a 37.17 (b	0.35 (a 0.31 (b	4
Selected values	132.4	37.2	0.35 (a 0.31 (b	

1. Olszewski: Compt. rend., 99, 184 (1884).
2. Wroblewski: Wied. Ann., 26, 134 (1885)
3. Witkowski: Phil. Mag., 41, 288 (1896)
4. Kuenen and Clark: Comm. Leyden. 150b, 1917; Proc. Acad. Sci. Amsterdam 19 II, 1088 (1917)

a) "Plait-point".
b) "Critical point of contact".

Wroblewski observed that near its critical point air behaves differently from other substances. This he ascribed to the fact that air is a mixture, although Kuenen and Clark believe that the special phenomena which he describes were largely due to insufficient mixing.

It is quite difficult to make determinations of the critical constants of air because of the fact that mercury can not be used directly for varying the pressure at these low temperatures. In its place the air itself is connected by means of a capillary tube to the outside measuring apparatus, and unless special care is used the air fractionates to some extent through the capillary and leaves the residue richer in oxygen.

In the case of certain binary mixtures there are, according to Kuenen[1], two critical points, the "critical point of contact" and the "plait point". The temperature of the "critical point of contact" corresponds to the critical temperature of a pure substance as defined in the first part of the paper in that this temperature is the highest at which liquid can exist at any pressure. The liquid condensing just below this temperature differs in composition from the

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[1] Kuenen: Comm. Leyden No. 4, 1892.

vapor phase and has a different density. At a somewhat lower temperature, the densities of the liquid and vapor phases become equal and the critical phenomena appear. This point is called the "plait point".

Kuenen and Clark, however, do not make themselves entirely clear in this respect, inasmuch as their data and curve indicate that the densities are equal at the "critical point of contact" and not at the "plait point".

The air was free from water vapor and carbon dioxide. The pressures were measured in a closed hydrogen manometer, while two platinum resistance thermometers were used for temperature measurements.

The density determinations were somewhat irregular and are considered uncertain.

Allylene

Date	T_c	Obs.
1905	402.6	1
1921	401.0	2
Selected value	401	

1. Lespieau and Chavanne: Compt rend., **140**, 1035 (1905).
2. Maass and Wright: J. Am. Chem. Soc., **43**, 1078 (1921)

Lespieau and Chavanne prepared allylene from propylene bromide and alcoholic sodium hydroxide. The precipitate formed by passing the gas through a solution of cuprous ammonium chloride was washed and treated with warm dilute hydrochloric acid. The allylene so obtained was washed with water and dried first over calcium chloride and then over fused potassium hydroxide. The gas was then passed through a bulbed tube maintained at −23°C. The allylene was then solidified and any residual gas removed by evacuation. A part of the allylene was distilled into another tube and used for the determination. The purity of this sample was somewhat questionable, especially in view of the fact the purity was checked by measuring the volume changes occurring when 2.5 cc of the allylene was exploded with air and the carbon dioxide produced was absorbed with potassium hydroxide. The critical temperature was taken as the lowest temperature of appearance or disappearance of an image formed by reflection on the surface of the liquid enclosed in a sealed tube.

The details of the method used by Maass and Wright for the preparation of allylene are to be published in connection with another investigation. Exceptional purity, however, is claimed for the samples used and preference is therefore given to the value obtained by these authors.

Centnerszwer and the later observers have agreed fairly well on the critical temperature of ammonia excepting, perhaps, Cardoso and Giltay whose result is a little higher than the others.

All of the observers took great care in the purification of their samples and there is no one observer to whose work a preference can be given. It therefore seems best to average the results for the critical temperature extending as far back as that of Centnerszwer.

Ammonia

Date	T_c	P_c	d_c	Obs.
1884	403.1*	115.0*		1
1886	404.1	113.0		2
1903	405.63			3
1908	405.4			4
1910	405.2	111.3		5
1912	406.0	112.3		6
1913	405.3			7
1918	405.4		0.2364	8
1918	405.4		0.2362	9
Selected value	405.5	112	0.236	

1. Dewar: Phil. Mag., 18, 210 (1884)
2. Vincent and Chappuis: J. phys., 5, 58 (1886); Compt. rend., 103, 379 (1886)
3. Centnerszwer: Z. physik Chem., 46, 456 (1903).
4. Jaquerod: Mem. Soc. phys. genève 35, 686 (1908).
5. Scheffer: Z. physik Chem., 71, 695 (1910).
6. Cardoso and Giltay: J. chim. phys., 10, 514 (1912)
7. Estreicher and Schnerr: Z. komprimierte flüssige Gase Pressluft-Ind., 15, 161 (1913).
8. Berthoud: J. chim. phys., 16, 434 (1918)
9. Berthoud: Helvetica Chim. Acta, 1, 84 (1918).

Since the two recent determinations of the critical pressure differ by one atmosphere, the whole number nearer the mean is selected.

Berthoud is the only observer who has determined the critical density. He measured the densities of the liquid and vapor phases using the method of Young modified by Ter Gazarian[1]. The value for the densities of the two phases when equal was taken as the critical density.

Argon

Date	T_c	P_c	d_c	Obs.
1895	152.1	50.6		1
1901	155.7	52.9		2
1910	150.66	47.996	0.509 (a	3
1912			0.53078 (b	4
Selected values	150.7	48.0	0.52	

1. Olszewski: Trans. Roy. Soc. London 186A, 253 (1895)
2. Ramsay and Travers: Trans. Roy. Soc. London, 197A, 87 (1901)
3. Crommelin: Comm. Leyden. Nos. 115, 118a (1910)
4. Mathias, Onnes and Crommelin: Comm. Leyden No. 131a (1912); Proc. Acad. Sci. Amsterdam, 15, II, 961 (1913); Ann. phys., 17, 442 (1922)

a) from equation $\left\{\frac{dP}{dT}\right\}_v = \left\{\frac{dP}{dT}\right\}_{coex.}$

b) from rectilinear diameter

The argon used by Olszewski was not sufficiently pure to justify a serious consideration of his work in comparison with later observations. Ramsay and

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[1] J. chim. phys., 4, 140 (1906)

Travers obtained their critical pressures from vapor pressure curves as interpolated by the rule of Ramsay and Young[1] and their cryostat was rather crude.

Crommelin extracted argon from the air by absorbing the oxygen and nitrogen with a mixture of calcium carbide and calcium chloride (method of Fischer and Ringe[2]). It was then purified by passing over the mixture of quicklime, magnesium and sodium, recommended by Hempel[3].

The temperatures were measured by means of a platinum resistance thermometer which had been compared with a hydrogen thermometer. Crommelin did not make an exact determination of the critical constants because he suspected that his argon was not pure, but probably contained traces of nitrogen. In addition his cryostat did not maintain sufficiently constant temperatures. The two values for the critical density were calculated by Crommelin by two different methods, the mean being used as the best value.

Isobutane, Normal Butane

Compound	T_c	P_c
Isobutane	406.8	36.54
Normal Butane	426.3	35.67

Seibert and Burrell[4] made the only determinations on the compounds isobutane and normal butane.

Isobutane was prepared by the action of a zinc copper couple upon isobutyl iodide and collected over potassium hydroxide. It was then solidified by liquid air and all remaining gases were removed by evacuating. The gas was fractionated ten times to remove any normal butane. It was later fractionated several times at −98°.

Normal butane was prepared from n-butyl iodide and the zinc copper couple, collected over potassium hydroxide and purified by fractionation.

Each of these gases could be liquefied completely at constant temperature without an appreciable increase of pressure. Several other tests indicated that they were of quite high purity.

The critical temperature was taken as that at which no meniscus was visible when the volume was constant, but just appeared when the volume was slightly increased. Duplicate experiments never differed by more than 0.1°. The pressures were measured by a calibrated air manometer.

The determinations of the critical temperature of carbon dioxide all agree remarkably well with the exception of the value given by Sarrau, which was calculated from temperature-pressure-volume data. Dewar and Chappuis merely give the figures attributed to them without stating the sources. The

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[1] Phil. Mag. (5) **20**, 515 (1885); **21**, 33; **22**, 37 (1886)

[2] Ber., **41**, 2017 (1908).

[3] "Gasanalytische Methoden," 3d Ed., p. 150.

[4] J. Am. Chem. Soc., **37**, 2683 (1915)

direct determinations of the critical temperature, especially the latest ones, indicate that 304.1° can be safely assumed to be correct within 0.1°.

The earlier determinations of the critical pressure were high. This, however, is to be expected considering that equilibrium is rather hard to obtain, especially if even slight amounts of impurities are present.

Carbon Dioxide

Date	T_c	P_c	d_c	Obs.
1869	304.2	73.0		1
1876	304.02	77.0	0.30	2
1881	304.1*			3
1882	(305.1)	(77.0)	(0.4395)	4
1884	305.0*	77.0*	(0.65)	5
1886			0.46	6
1892	304.45	72.9	0.464	7
1894	304.5			8
1896	304.1			9
1903	304.05			10
1903	304.08	72.93	0.469	11
1904	304.22			12
1906	304.085		0.460	13
1912	304.1±.1	72.85±.1		14
Selected values	304.1	72.9	0.460	

1. Andrews: Trans. Roy. Soc. London, **159** II, 575 (1869)
2. Andrews: Trans. Roy. Soc. London, **166** II, 421) 1876)
3. Hautefeuille and Cailletet: Compt. rend., **92**, 840 (1881)
4. Sarrau: Compt. rend., **94**, 718 (1882)
5. Dewar: Phil. Mag., **18**, 210 (1884)
6. Cailletet and Mathias: Compt. rend., **102**, 1202 (1886)
7. Amagat: Compt. rend., **114**, 1093 (1892)
8. Chappuis: Compt rend., **118**, 976 (1894)
9. Verschaffelt: Zitt. Versl (1896)
10. Von Wesendonck: Verh. deutsch Phys. Ges., **5**, 238 (1903)
11. Keesom: Comm. Leyden No. 88 (1903)
12. Brenkmann: Dissertations Amsterdam (1904)
13. Onnes and Fabius: Comm. Leyden No. 98 (1906)
14. Cardoso and Bell: J. chim. phys., **10**, 500 (1912)

Keesom and Cardoso and Bell agree very well on the critical pressure, which may be taken as 72.9 atm.

The latest value for the critical density is that of Onnes, who gives 0.460. This is a correction of Keesom's value of 0.469. The determinations of the critical temperature and pressure made by Andrews in 1869 are remarkably close to the selected figures.

The only determinations of which the details have been published are those of Cardoso. Neither Olszewski nor Onnes states where he obtained the figures which they used in their calculations.

Cardoso prepared carbon monoxide from formic acid and sulphuric acid and passed the gas through potassium hydroxide and phosphorus pentoxide, testing for purity in the usual way, by observing the pressure during condensation.

Carbon Monoxide

Date	T_c	P_c	d_c	Obs.
1884	133.6	35.5		1
1913	132.0	35.9		2
1915	134.4	34.6	0.3110	3
Selected values	134.4	34.6	0.3110	

1. Olszewski: Compt. rend., 99, 706 (1884); Wied. Ann. **31**, 66, 70 (1887)
2. Onnes, Mathias and Crommelin: Proc. Acad. Sci. Amsterdam, **5 II**, 1401 (1913) Comm. Leyden No. 134 c
3. Cardoso. Arch. sci. phys. nat., 39, 400 (1915)

Estreicher and Schnerr and Pellaton have made the only recent determinations of the critical constants of chlorine and their values for the critical temperature differ from each other by 0.8°.

Pellaton prepared chlorine by the decomposition of gold chloride. Specially purified gold was heated electrically to 300°C in a stream of air to remove moisture, and was chlorinated at 200°. The laboratory tubes were evacuated to 0.005 mm while heated with a Bunsen burner and the chlorine evolved by heating the gold chloride was condensed in them.

Chlorine

Date	T_c	P_c	d_c	Obs.
1878	421.1			1
1884	414.1*	83.9		2
1890	419.1	93.5		3
1913	416.3			4
1915	417.1	76.1	0.573	5
Selected values	417	76	0.573	

1. Ladenburg: Ber., **11**, 818 (1878)
2. Dewar: Phil. Mag., **18**, 210 (1884)
3. Knestach: Ann., **259**, 100 (1890)
4. Estreicher and Schnerr: Z. komprimierte flüssige Gase Pressluft-Ind., **15**, 161 (1913)
5. Pellaton: J. chim. phys., **13**, 426 (1915)

The tubes were detached with a blow-pipe and the critical constants determined in the usual way by noting the appearance and disappearance of the meniscus.

The thermometer was calibrated at 100°, 130°, and 154° by means of water, chlorobenzene and bromobenzene.

The thermostat which was immersed in a second thermostat maintained the temperatures constant to 0.01°.

The above work was very carefully carried out and because the description of the details of Estreicher and Schnerr's work could not be obtained, preference is given to the values of Pellatin, choosing 417° as the critical temperature.

Cyanogen

Date	T_c	P_c	Obs.
1884	397.1*	61.7*	1
1910	401.4	59.6	2
1912	401.4	59.75	3
1913	399.65	58.2	4
Selected values	401.4	59.7	

1. Dewar: Phil. Mag., **18**, 210 (1884)
2. Cardoso and Baumé: Compt. rend., **151**, 141 (1910)
3. Cardoso and Baumé: J. chim. phys., **10**, 511 (1912)
4. Crommelin (1913). Quoted in Tab. Ann. Int. de Constants et Données numériques, Vol. IV, 1st. Part, p. 292, 318

Cardoso and Baumé prepared cyanogen from mercuric cyanide and mercuric chloride. The gas was dried over phosphorus pentoxide, condensed by means of liquid air and fractionated about nine times.

Near the critical temperature cyanogen changes partly into paracyanogen but these experimenters regard the solubility of paracyanogen in liquid cyanogen as too slight to change the critical constants of the latter.

The reference to Crommelin is given in the Tab. Ann. Int. de Constants as Proc. Acad. Sci. Amst. 1913, but no such article upon cyanogen appears in this volume nor has any reference to work upon this gas by Crommelin been found in the literature.

Cardoso and Baumé's values are therefore accepted. No determinations of the critical density have been found.

Kuenen, who was the first to make very accurate measurements of the critical constants of ethane, prepared his sample by the electrolysis of a concentrated solution of sodium acetate. The gas was washed in sulphuric acid and sodium hydroxide solution. It was then passed through fuming sulphuric acid, caustic potash, and phosphorus pentoxide, after which it was liquefied and distilled. The laboratory tube was provided with an electromagnetic stirrer to insure equilibrium. That the ethane still contained traces of impurity was indicated by the fact that the pressure increased 0.43 atm. when the vapor was condensed at constant temperature. No details regarding the method used for determining the critical density were given.

The ethane used by Cardoso and Bell was prepared by two methods, namely that of Grignard and that of Frankland and Kolbe. In the former method ethyl iodide dissolved in dry ether was slowly added to pure magnesium covered with ether. The gas was liquefied, then distilled and passed through alcoholic potassium hydroxide, bromine water, and concentrated sulphuric acid. This cycle was repeated seven times after which the gas was purified from air by nine fractionations. The second method consisted of slowly adding ethyl cyanide to sodium wire, the evolved gas being passed through potassium hydroxide, sulphuric acid, and finally phosphorus pentoxide. The measurements made upon the ethane prepared by the two methods checked very closely.

Ethane

Date	T_c	P_c	d_c	Obs.
1884	308*	45.2		1
1889	307	50.2		2
1894	305-313	50		3
1895	305.3			4
1897	305	48.8		5
1902	305.05	48.43	0.206	6
1913	305.2±.1	48.85		7
1915	305.42	48.13		8
Selected values	305.2	48.8	0.21	

1. Dewar: Phil. Mag., **18**, 210 (1884)
2. Olszewski: Bull. intern. l'acad. sci. Cracovie, 27 (1889); Phil. Mag., **39**, 210 (1895)
3. Haenlin: Ann. **282**, 236, 245 (1894)
4. Kuenen: Comm. Leyden No. 16 (1895)
5. Kuenen: Phil. Mag., **44**, 195 (1897)
6. Kuenen: Phil. Mag., **3**, 628 (1902)
7. Cardoso and Bell: J. chim. phys., **10**, 497 (1913)
8. Prins: Proc. Acad. Sci. Amsterdam, **17**, II, 1095 (1915)

Prins prepared ethane by electrolyzing a sodium acetate solution. The gas was purified by bromine water and a strong solution of potassium hydroxide, dried over soda lime and condensed by liquid air. Subsequently it was dried over phosphorus pentoxide and fractionated by the use of liquid air. The disappearance of the discharge in a Geissler tube attached to the apparatus served as a criterion of purity. The details of making the determinations

Ethyl Chloride

Date	T_c	P_c	Obs.
1859	457.2*		1
1878	455.8*	52.6*	2
1884	463.0		3
1886	455.6	54	4
Selected values	456 ?	54 ?	

1. Drion: Ann. chim. phys., **56**, 221 (1859)
2. Sajotschewsky: Kiewer Univers. Unters (1878); Beibl. Ann. Physik., **3**, 741 (1879)
3. Jouk: J. Russ. Phys. Chem. Soc., **16**, 304 (1884); Beibl. Ann. Physik., **8**, 808 (1884)
4. Vincent and Chappuis: J. phys., **5**, 58 (1886)

of the critical constants were not stated other than that the Cailletet method was used. The values obtained by Cardoso and Bell agree very well with those of Kuenen and are preferred to the values of Prins because of the care with which the determinations were made.

None of the values for ethyl chloride is reliable. Vincent and Chappuis do not state how they prepared their sample and the others merely quote their figures.

Until more measurements are made it seems best to use the values by Vincent and Chappuis, taking 456° for the critical temperature.

Ethylene

Date	T_c	P_c	d_c	Obs.
1880	282.3	58	0.36	1
1882	286			2
1882	(274.6)	(43.5)	(0.187)	3
1884	283.2*	51.0		4
1886			0.22	5
1895	283.0	51.7		6
1912	282.6±.1	50.65±.1		7
1921	283.0±.2			8
Selected values	282.6	50.7		

1. Van der Waals: Beibl. Ann. Physik, **4**, 704 (1880)
2. Cailletet: Compt. rend., **94**, 1224 (1882)
3. Sarrau: Compt. rend., **94**, 845 (1882)
4. Dewar: Phil. Mag., **18**, 210 (1884)
5. Cailletet and Mathias: Compt. rend., **102**, 1202 (1886)
6. Olszewski: Phil. Mag., **39**, 203 (1895)
7. Cardoso and Arni: J. chim. phys., **10**, 505 (1912)
8. Maass and Wright: J. Am. Chem. Soc., **43**, 1098 (1921)

The only recent determinations of the critical constants of ethylene are those of Cardoso and Arni and of Maass and Wright.

Cardoso and Arni prepared ethylene from sulphuric acid and ethyl alcohol, passed the gas through two columns of solid potassium hydroxide, two bulbs of concentrated sulphuric acid, and dried it ever phosphorus pentoxide, after which it was fractionated ten times.

The ethylene used by Maass and Wright was prepared by the dehydrating action of aluminum oxide upon purified ethyl alcohol at a temperature of 350°C. The gas was then purified by several distillations, a final purification being obtained by distilling five times in a vacuum, the middle portions being retained in each instance. The temperatures were measured by a platinum resistance thermometer for which an accuracy of 0.2° was claimed. These authors, however, do not state how the critical constants were obtained and preference is therefore given to the value by Cardoso and Arni, although the difference between their observations and those of Maass and Wright is not large.

The determinations of the critical density are all old values and can not be relied upon.

An accuracy of 0.1° is claimed for the value which Onnes gives for the critical temperature of helium. The critical pressure given is the lower limit; the true value is believed by Onnes to be slightly higher. The critical density was derived indirectly from the densities of co-existing liquid and saturated vapor by the method described in Leyden Comm. No. 119.

Helium

Date	T_c	P_c	d_c	Obs.
1911	5.25	2.26	0.066	1
1915	5.20	2.26		2
Selected values	5.20	2.26	0.066	

1. Onnes: Comm. Leyden No. 124b (1911); Proc. Acad. Sci. Amsterdam, **14**, 678 (1912)
2. Onnes and Weber: Comm. Leyden 147b (1915); Proc. Acad. Sci. Amsterdam, **18**, 506 (1916)

Considering the great difficulty in reaching such low temperatures as are necessary, it is not surprising that even the recent determinations of the critical constants of hydrogen do not agree.

The first experimental measurements of the critical constants of hydrogen were made by Olszewski in 1895. He used oxygen boiling under reduced

Hydrogen

Date	T_c	P_c	d_c	Obs.
1882	(98.9)	(98.9)	(0.050)	1
1885	(32.7)	(13.3)		2
1895	38.6	20.0		3
1899	52*	19.4*		4
1905	32.3	13.4—15.0		5
1913	31.95	11.0		6
1917	33.18	12.80	0.0310	7
1921			0.03102	8
Selected values	33.18	12.8	0.0310	

1. Sarrau: Compt. rend., **94**, 845 (1882)
2. Wroblewski: Sitz. Akad. Wiss. Wien., **91**, (1885); **97**, 1362 (1888)
3. Olszewski: Phil. Mag., **39**, 202 (1895)
4. Dewar: Proc. Roy. Soc. (London) **64**, 227 (1899)
5. Olszewski: Ann Physik., **17**, 986 (1905)
6. Bulle: Physik. Z., **14**, 860 (1913)
7. Onnes, Crommelin and Cath. Proc. Acad. Sci. Amsterdam, **20**, 178 (1917); Comm. Leyden No. 151c
8. Mathias, Crommelin and Onnes: Comm. Leyden No. 154 (1921); Ann. phys., **17**, 463 (1922)

pressure as a cooling agent but was unable to reach a sufficiently low temperature. Upon expanding the gas from pressures of 80–140 atms. he found that the phenomenon of ebullition occurred always at 20 atms. Although he observed that if the initial pressure was 70, 60, and 50 atms., the ebullition appeared at a lower and lower pressure, viz., approximately 18, 16, and 14 atms., nevertheless he chose 20 atms. as the critical pressure. He then, by means of a platinum resistance thermometer, measured the temperature attained upon expanding to 20 atms. where ebullition occurred, and assumed this to be the critical temperature.

In 1905 he determined the constants by a greatly improved method, using liquid hydrogen as the cooling medium. Upon observing the meniscus he found that it appeared at 13.4 atm. and disappeared at 15 atm.

The work of Bulle followed in 1913, but according to Onnes it seems unlikely that the temperatures within the apparatus were uniform.

Onnes[1] and his coworkers developed a special cryostat with which they were able to maintain very constant temperatures. Because of this improved apparatus and also the care with which the work was done, their results are probably the most accurate thus far obtained.

Hydrogen Bromide

Date	T_c	Obs.
1896	364.4	1
1910	364.1	2
1919	362.9	3
Selected values	363.5 ?	

1. Estreicher: Z. physik. Chem., **20**, 605 (1896)
2. Estreicher and Schnerr: Z. Komprimierte flüssige Gase Pressluft-Ind., **15**, 161 (1913); Dissertations Amsterdam (1910)
3. Moles: J. chim. phys., **17**, 421 (1919)

They purified their hydrogen by distillation and made carfeul determinations of a number of isothermals, the temperatures being measured by means of a helium thermometer. By connecting the points which gave the beginning and completion of the liquefaction, a parabola was obtained and the pressure corresponding to the top of this parabola was taken as the critical pressure. The corresponding temperature was found by extrapolation from the vapor pressure measurements immediately below the critical temperatures.

The heterogeneous parts of these isothermals were accurately parallel to the axis, which shows that the purity of the sample was very high.

The critical density was calculated by means of the law of Cailletet and Mathias[2], using the density data previously published.

It is interesting to note how remarkably close Wroblewski's calculated values for the critical temperature and pressure come to the experimental ones.

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[1] Comm. Leyden No. 154c; Proc. Acad. Sci. Amsterdam, **23 II**, 1185 (1922)
[2] Comm. Leyden Nos. 127c and 137

Moles considers that Estreicher's earlier value was obtained with a somewhat impure sample. Moles prepared hydrogen bromide from metaphosphoric acid and potassium bromide. The gas was liquefied and purified by boiling and condensing in small laboratory tubes.

The value chosen is the mean of the last two determinations and is of doubtful accuracy.

Owing to the fact that hydrogen bromide reacts with mercury, a mercury manmeter can not be used to measure the pressures. No determinations of critical pressure have been published to date.

Hydrogen Chloride

Date	T_c	P_c	d_c	Obs.
1879	324.35	86		1
1884	325.4*	86*	(0.61)	2
1886	324.6	96		3
1897	325.1 ± .5	83 ± 1		4
1906	324.9 ± .2	83.6 ± .4		5
1910	324.5			6
1912	324.5 ± .1	85.55 ± .15		7
1913	324.1	80.49		8
Selected values	324.5	83 ?		

1. Ansdell: Chem. News, **41**, 75 (1880)
2. Dewar: Phil. Mag., **18**, 210 (1884)
3. Vincent and Chappuis: J. phys., **55**, 58 (1886)
4. Leduc and Sacerdote: Compt. rend., **125**, 397 (1897)
5. Briner: J. chim. phys., **4**, 476 (1906)
6. Estreicher and Schnerr: Z. komprimierte flüssige Gase Pressluft-Ind., **15**, 161 (1913); Dissertations Amsterdam (1910)
7. Cardoso and Germann: J. chim. phys., **10**, 517 (1912)
8. Drozdowski and Pietrzak: Anz. Akad. Wiss. Krakau, **4**, (1913).

The various observers agree quite well regarding the critical temperature of hydrogen chloride, but their results on the critical pressure deviate widely.

The only criterion of the purity of Leduc and Sacerdote's sample, which was prepared from sulphuric acid and sodium chloride, was that of complete absorption by water.

Briner does not describe his method, while the articles by Estreicher and Schnerr and by Drozdowski and Pietrzak could not be obtained.

Cardoso and Germann used concentrated sulphuric acid and pure precipitated sodium chloride, and passed the gas through five bottles of concentrated sulphuric acid and a tube of phosphorus pentoxide. The hydrogen chloride was then distilled ten times, and passed over phosphorus pentoxide after each of the first six fractionations.

The value 324.5° is selected as the most reliable for the critical temperature. Because of the great divergence of the values for the critical pressure a mean of 83 atm. is selected. No reliable figure for the critical density has been published.

Estreicher's first determination of the critical temperature of hydrogen iodide was made with a sample prepared by the action of red phosphorus upon a mixture of pulverized iodine and water. After the removal of most of the iodine vapor with water, the gas was dried with phosphorus pentoxide and solidified by means of a mixture of solid carbon dioxide and ether. The remaining iodine was removed by distillation. According to these determinations which were made in a sealed tube, the meniscus disappeared at 150.7° and appeared again at 150.4°.

Hydrogen Iodide

Date	T_c	Obs.
1896	423.8	1
1910	423.9	2
Selected value	423.9	

1. Estreicher: Z. physik. Chem., 20, 605 (1896)
2. Estreicher and Schnerr: Z. komprimierte flüssige Gase Pressluft-Ind., 15, 161 (1913); Dissertations Amsterdam (1910)

This value was later checked to 0.1° by Estreicher and Schnerr and constitutes the only available work upon the critical constants of this gas.

Scheffer prepared hydrogen sulphide by the action of dilute sulphuric acid on a sodium hydrosulphide solution containing barium sulphide, and purified the gas by fractionating. His determinations were not carried out with as many precautions as those of the later observers.

Cardoso and Arni prepared their samples from hydrochloric acid and pure precipitated ferrous sulphide. The gas was passed through a suspension of ferrous sulphide in water and thence over calcium chloride and phosphorus pentoxide after which it was distilled fourteen times.

Hydrogen Sulphide

Date	T_c	P_c	Obs.
1884	373.3*	92*	1
1890	373.1	88.77	2
1897	373.1±.5	90	3
1910	372.7	88.3	4
1910	373.53		5
1912	373.5±.1	89.05±.1	6
Selected values	373.5	89	

1. Dewar: Phil. Mag., 18, 210 (1884)
2. Olszewski: Beibl. Ann. Physik., 14, 896 (1890)
3. Leduc and Sacerdote: Compt. rend., 125, 397 (1897)
4. Scheffer: Z. physik. Chem., 71, 695 (1910)
5. Estreicher and Schnerr: Z. komprimierte flüssige Gase Pressluft-Ind., 15, 161 (1913); Dissertations Amsterdam (1910)
6. Cardoso and Arni: J. chim. phys., 10, 504 (1912)

They found that all the mercury as well as the gas had to be very carefully dried, otherwise a slight decomposition would take place which proceeded apparently until a definite small pressure of hydrogen was produced.

Because of the care with which their work was carried out and the close check obtained by Estreicher and Schnerr, their value for the critical temperature is considered the best.

Preference is given to Cardoso and Arni's value for the critical pressure.

No determinations of the critical density have been made.

Krypton

Date	T_c	P_c	Obs.
1901	210.6	54.3	1
Selected values	210.6 ?	54.3 ?	

1. Ramsay and Travers: Trans. Roy. Soc. London **197**, 87 (1901)

The only determinations of the critical constants of krypton are those of Ramsay and Travers. They separated this gas from oxygen, nitrogen and xenon by repeated fractionations, but because of the small quantities of gas with which they had to deal it is doubtful whether their samples were very pure.

Methane

Date	T_c	P_c	d_c	Obs.
1882	(197.4)	(46.8)	0.145	1
1884	199.6	56.8		2
1884	173.6*	50*		3
1885	191.3	54.9		4
1913	190.25	45.60±.05	0.1623	5
1915			0.1623	6
1922	191.03	45.79	0.1613	7
Selected values	190.6 ?	45.7	0.162	

1. Sarrau: Compt. rend., **94**, 718 (1882)
2. Wroblewski: Compt. rend., **99**, 136 (1884)
3. Dewar: Phil. Mag., **18**, 210 (1884)
4. Olszewski: Compt. rend., **100**, 940 (1885)
5. Cardoso: Arch. sci. phys. nat., **36**, 97 (1913)
6. Cardoso: Arch. sci. phys. nat., **39**, 403 (1915)
7. Keyes, Taylor and Smith: J. Math. and Phys., Mass Inst. Tech. **1** 211 (1922)

Cardoso does not give any details as to his method of preparation of methane, but the purity of his sample was very high as indicated by the fact that upon condensation at constant temperature the pressure remained constant to about 0.01 atm.

Keyes, Taylor, and Smith used methane prepared by heating a mixture of dry sodium acetate and soda lime. Any acetone formed was absorbed by 20 per cent fuming sulphuric acid, the sulphur trioxide fumes being removed by

98 per cent concentrated sulphuric acid. The gas was passed through a caustic soda solution and then over solid caustic and phosphorus pentoxide. Further purification was obtained by fractional distillation. The impurities were not in excess of one part in five hundred. The critical constants, ti is stated, were directly observed, but the method is not described. The sample was not stirred during the determination. The critical pressure given by these authors in Table I (p. 223) as the observed value is 46.06, the value 45.8 being calculated from the vapor pressure formula.

Cardoso's values for the vapor pressure were found to be uniformly higher than those of Keyes and his coworkers by an amount corresponding to a temperature difference of 0.56°, and these authors therefore assume that Cardoso's temperature measurements are low by this amount. On the other hand in a footnote (p. 226) it is apparent that Cardoso's fixed point, the freezing point of toluene is too high. This contradiction taken together with the statement on a preceding page that the higher vapor pressures were not very concordant because of lack of sufficient stirring would throw doubt upon the validity of the proposed correction.

The critical constants selected are the means of these two recent sets of observations.

Methyl Chloride

Date	T_c	P_c	d_c	Obs.
1886	414.6	73		1
1893	416.1	65.0		2
1904	416.1±.2		0.370	3
1904	416.22	65.93		4
1906	416.3	65.85		5
Selected values	416.2	65.9	0.37 ?	

1. Vincent and Chappuis: Compt. rend., **100**, 1216 (1885); **103**, 379 (1886)
2. Kuenen: Arch. néerl., **26**, 368 (1893)
3. Centnerszwer: Z. physik. Chem., **49**, 203 (1904)
4. Brinkmann: Dissertations Amsterdam (1904)
5. Baumé: J. chim. phys., **6**, 1 (1908)

The recent determinations on methyl chloride agree quite well.

Centnerszwer purified his sample by passing over soda lime, calcium chloride, and sulphuric acid, after which it was distilled into the tubes. No variation in pressure was observed when the gas was condensed at constant temperature. He did not agitate the gas while making the determinations.

Baumé passed the methyl chloride through sulphuric acid and fractionated it five or six times.

The results of these observers are averaged with those of Brinkmann.

The values which Centnerszwer obtained for the density by the method of Cailletet and Mathias varied, within 0.01° of the critical temperature, from

0.3397 to 0.3790. When it is considered that his figure for the critical temperature may be in error by 0.2°, it is unlikely that the value for the critical density is accurate to even the second significant figure.

Neon

Date	T_c	P_c	Obs.
1917	44.74	26.86	1
Selected values	44.7	26.9	

1. Onnes, Crommelin and Cath: Comm. Leyden No. 151b (1917); Proc. Acad. Sci. Amsterdam, 19, 1058 (1917)

Onnes, Crommelin and Cath have made the only published determination of the critical constants of neon. The impure gas which they had at their disposal was freed from hydrogen by explosion with oxygen. It was then repeatedly frozen and distilled over carbon cooled in liquid air. Traces of impurities still remained, however, as indicated by the increase of 0.2 atm. pressure when the gas was liquefied at constant temperature; and because of these impurities the values for the critical temperature and critical pressure are believed by Onnes and his coworkers to differ from the true values by a few tenths of a unit. The temperatures were measured with a helium thermometer.

Vapor pressure measurements were made and the apparatus was so arranged that the quantities of gas which were liquefied at a given temperature between the beginning and the end of condensation could be measured. Using the values obtained in this manner at different temperatures in the neighborhood of the critical temperature the critical constants were calculated by extrapolation over a small range.

Nitric Oxide

Date	T_c	P_c	Obs.
1885	179.6 ?	71.2 ?	1
Selected values	180?	71 ?	

1. Olszewski: Compt. rend., 100, 940 (1885)

The only determination of the critical constants of nitric oxide is that of Olszewski in 1885. The gas was prepared by boiling ferrous sulphate with dilute nitric acid. The gas was liquefied in a part of the apparatus which had been previously evacuated. Olszewski found the meniscus still visible at 179.6° and 71.2 atm., but owing to his fear that the tube might burst he did not raise the temperature or pressure further. His sample was not well purified and it can be seen from the results on other gases that his determinations of this early date are not in accord with those by later observers.

The nitrogen used by Onnes, Dorsman and Holst was prepared by boiling a solution of sodium nitrite and sodium sulphate with ammonia. The gas was passed over sulphuric acid to remove the ammonia. During condensation at constant temperature there was no appreciable increase in pressure so that the gas may be considered as quite pure.

·Nitrogen

Date	T_c	P_c	d_c	Obs.
1882	(149.3)	(42.1)	(0.2719)	1
1884	127	35		2
1884	127*	35*	(0.45)	3
1885	127	33		4
1886			0.44	5
1914	125.96	33.49		6
1914			0.31096	7
1916	128.4	33.65		8
Selected values	126.0	33.5	0.3110	

1. Sarrau: Compt. rend., 94, 718 (1882)
2. Olszewski: Compt. rend., 99, 133 (1884); Ann. Physik., 31, 66, 70 (1887); Phil. Mag., 39, 210 (1895).
3. Dewar: Phil. Mag., 18, 210 (1884)
4. Wroblewski: Wien. Ber., 91, 696 (1885); 92, 641 (1885)
5. Wroblewski: Compt. rend., 102, 1010 (1886)
6. Onnes, Dorsmann and Holst: Comm. Leyden No. 145b (1914) Proc. Acad. Sci. Amsterdam, 17 II, 950 (1915)
7. Mathias, Onnes and Crommelin: Comm. Leyden No. 145c (1914) Ann. phys., 17, 455 (1922)
8. Cardoso: J. chim. phys., 13, 312 (1915)

Cardoso's sample was obtained by heating pure potassium nitride and passing the gas over pure calcined barium oxide, followed by drying over phosphorus pentoxide. The purity was checked by the vapor pressure method.

As in the case of oxygen the values of Onnes rather than those of Cardoso are accepted although this choice may be questioned.

The value for the critical density obtained by Mathias is the only determination available and is probably quite accurate.

The nitrous oxide prepared by Villard was evidently very pure judging from the regular phenomena obtained near the critical point, but his values were obtained indirectly by measuring the densities of the liquid and gas phases.

Kuenen purified commercial nitrous oxide by passing it over calcium chloride, caustic potash, and phosphorus pentoxide after which it was liquefied and distilled. The increase of 0.15 atm. pressure when condensed at constant temperature indicated a slight impurity.

The samples used by Cardoso and Arni were prepared from hydroxylamine hydrochloride and sodium nitrite solution and purified by passing through potassium hydroxide solution, sulphuric acid and finally phosphorus pentoxide.

The gas thuse obtained was fractionated ten times. Their values are no doubt the best. Because of the apparent high purity of his nitrous oxide, preference is given to Villard's value for the critical density. More data, however, are needed to corroborate this figure.

Nitrous Oxide

Date	T_c	P_c	d_c	Obs.
1878	309.5	73.07		1
1884	308.5*	75*		2
1886			0.41	3
1894	311.9	77.5	0.454	4
1897	309.1	71.9		5
1912	309.6	71.65		6
Selected values	309.6	71.7	0.45 ?	

1. Janssen: Beibl. Ann. Physik. **2**, 136 (1878)
2. Dewar: Phil. Mag., **18**, 210 (1884)
3. Cailletet and Mathias: Compt. rend., **102**, 1202 (1886)
4. Villard Compt. rend., **118**, 1096 (1894); J. phys., **3**, 441 (1894)
5. Kuenen: Phil. Mag., **44**, 195 (1897)
6. Cardoso and Bell: J. chim. phys., **10**, 505 (1912)

There have been only two determinations of critical temperature and pressure made upon oxygen since 1885, one by Onnes, Dorsmann and Holst and one by Cardoso, both published about the same time. Owing to the comparatively crude apparatus used in obtaining the earlier results, it is not surprising that they were largely in error.

The oxygen used by Onnes, Dorsman and Holst was prepared by heating pure recrystallized potassium permanganate in an apparatus made entirely

Oxygen

Date	T_c	P_c	d_c	Obs.
1882	(167.7)	(48.7)	(0.3637)	1
1884	160.1*	50*	(0.63)	2
1885	155.1	50		3
1885	154.3	50.8		4
1911			0.4299	5
1915	154.27	49.71		6
1915	155.1	49.3		7
Selected values	154.3	49.7	0.430	

1. Sarrau: Compt. rend., **94**, 639 (1882)
2. Dewar: Phil. Mag., **18**, 210 (1884)
3. Wroblewski: Ann. Physik., **25**, 401 (1885); Compt. rend., **97**, 309 (1883)
4. Oleszewski: Phil. Mag., **39**, 210 (1895); Compt. rend., **100**, 350 (1885)
5. Mathias and Onnes: Comm. Leyden No. 117 (1911); Proc. Acad. Sci. Amsterdam, **13**, (1911); Ann. phys., **17**, 416 (1922)
6. Onnes, Dorsman and Holst: Proc. Acad. Sci. Amsterdam, **17**, (1915); Comm. Leyden 145b
7. Cardoso: J. chim. phys., **13**, 312 (1916)

of glass and passing the gas over heated platinized asbestos. The gas was then cooled with liquid air and allowed to slowly evaporate, thereby eliminating carbon dioxide and water vapor. The sample showed a constant pressure while being condensed at constant temperature. The pressures above 20 atm. were measured by means of a closed hydrogen manometer.

As the critical point, Onnes and his coworkers took the point at which on a small expansion the meniscus appeared half way up the tube and where conversely as the temperature reestablished itself it disappeared again at the same level. They looked particularly for the critical opalescence but failed to find it.

The value for the critical density was obtained from the equation of the rectilinear diameter.

Cardoso also prepared his oxygen from pure crystallized potassium permanganate, and passed the gas over solid potassium hydroxide, phosphorus pentoxide, and then through a Liebig bulb with mercury to decompose the ozone.

Owing to the fact that Cardoso did practically all the work alone, he had some difficulty in keeping the temperature constant while making his observations. His temperature measurements which were made with a pentane thermometer are also open to question.

In consideration of the excellent means which Onnes had at his disposal for making these measurements preference is given to his results.

Phosgene

Date	T_c	Obs.
1919	456.±0.5	1

1. Hackspill and Mathieu: Bull. 25, 482 (1919)

The only determination of the critical temperature of phosgene is that of Hackspill and Mathieu. These observers removed sulphur compounds from the commercial product by fractional distillation and eliminated most of the chlorine by contact with mercury for 24 hours. Final traces of chlorine were removed by distillation. The sealed tube containing the phosgene was placed in a hole in the center of a cylindrical aluminum block which could be heated electrically. The sample could be observed through a slot in the block. The temperatures were measured by means of a thermometer placed in another hole near the center of the block. Measurements indicated that the temperatures at this point and at the place occupied by the tube containing the gas could be maintained equal within 0.1°.

The purity of the sample is not established and the method, while suitable for making approximate determinations at these temperatures, is not accurate.

Haenlin apparently made no effort to purify his sample of propane which he prepared by heating propyl iodide with aluminum chloride for 20 hours at 130°C. His test for purity, which consisted of an analysis of the gas by exploding with oxygen, did not necessarily prove the absence of impurities. The observations of the critical phenomena were made in a sealed tube, the critical pressure being obtained from the vapor pressure data. Haenlin observed that as the temperature was raised the meniscus became indistinct at 101°C and that at 110°C all optical difference between the liquid and gas disappeared. Upon cooling, the critical opalescence appeared at 102°C which he selected as the critical temperature.

Propane

Date	T_c	P_c	Obs.
1889	370	44	1
1895	375	45.8	2
1905	370.6	45	3
1921	368.7		4
Selected values	368.7	45	

1. Olszewski: Bull. Int. l'Acad. Sci. Cracovie, Jan. (1889); Phil. Mag. (5), 39, 188 (1895)
2. Haenlin: Ann. 282, 245 (1895)
3. Lebeau: Bull. 33, 1137 (1905)
4. Maass and Wright: J. Am. Chem. Soc., 43, 1098 (1921).

Lebeau prepared propane by allowing propyl or isopropyl iodide to react with a solution of sodium in liquid ammonia. No criteria of purity are given. The critical temperature was determined both by the Cailletet method and by the sealed tube method.

Maass and Wright obtained propane by the action of the zinc-copper couple on propyl iodide. The gas was purified by passing through spirals cooled to −78°C, then a number of times over the zinc- copper couple moistened with alcohol at 50°C until free from iodide, then through concentrated silver nitrate and concentrated alkali solutions, and was finally dried by phosphorus pentoxide and condensed. The propane was further purified by five distillations in a vacuum, the middle portions being retained in each instance. The method of determining the critical temperature is not described.

Propylene

Date	T_c	P_c	Obs.
1883	370		1
1915	363.7	45.34	2
1921	365.2±0.2		3
Selected values	364.5 ?	45.3	

1. Nadejdine: J. Russ. Phys. Chem., 15, 25 (1883); Beibl. Ann. Physik., 7, 678 (1883)
2. Seibert and Burrell: J. Am. Chem. Soc., 37, 2683 (1915)
3. Maass and Wright: J. Am. Chem. Soc., 43, 1098 (1921)

The value obtained by these authors is preferred to that obtained by Lebeau because of the precautions taken to insure the purity of the sample. On the other hand, the value for the critical pressure determined by Lebeau is probably more accurate than the values published by Olszewski and by Haenlin.

Nadejdine makes no statement regarding the purity of the propylene which he used.

Seibert and Burrell obtained propylene by dehydrating propyl alcohol with phosphorus pentoxide, collected the gas over caustic potash and purified it by fractionation at low temperatures. As stated in the discussion of butane, the critical temperature was taken as that at which no meniscus was visible when the volume was constant, but just appeared when the volume was slightly increased. The pressures were measured by a calibrated air manometer.

The propylene used by Maass and Wright was prepared by the catalytic action of aluminum oxide upon purified propyl alcohol at a temperature of 350°C. The gas was purified by the methods adopted in the case of ethylene.

Sulfur Dioxide

Date	T_c	P_c	d_c	Obs.
1859	430.1			1
1878	430-434			2
1879	428.5*	78.9*		3
1882	428.1*			4
1884	428.5*	78.9*		5
1887	429.1		0.52	6
1903	430.36±.2			7
1906	430.3	77.95		8
1912	430.25±.1	77.65±.1		9
1913	430.24			10
Selected values	430.3	77.7	0.52?	

1. Drion: Ann. chim. phys., **56**, 221 (1859)
2. Ladenburg: Ber., **11**, 818 (1878)
3. Sajoschewski: Beibl. Ann. Physik., **3**, 741 (1879)
4. Schuck: Beibl. Ann. Physik, **6**, 86 (1882)
5. Dewar: Phil. Mag., **18**, 210 (1884)
6. Cailletet and Mathias: Compt. rend., **104**, 1563 (1887)
7. Centnerszwer: Z. physik Chem., **46**, 427 (1903)
8. Briner: J. chim. phys., **4**, 474 (1906)
9. Cardoso and Bell: J. chim. phys., **10**, 502 (1912)
10. Hein: Z. physik. Chem., **86**, 409 (1913)

The two later values for the critical temperature differ by 1.5°, so that their mean which is the selected value may be in error by as much as 0.8°.

The only published experimental determination of the critical pressure which could be found is that of Seibert and Burrell.

The values for the critical temperature of sulfur dioxide obtained since 1887 agree remarkably well, none of the four deviating more than 0.06° from the mean of 430.3°. This figure can therefore be taken as being accurate to the nearest tenth of a degree.

Critical Constants of Gases

Gas	Critical Temperature °C Abs.[a]	Critical Pressure Atm.	Critical Density g per cc
Acetylene	309 ?	61.6	0.231
Air	132.4	37.2	0.35[b] 0.31[c]
Allylene	401		
Ammonia	405.5	112	0.236
Argon	150.7	48.0	0.52
Butane-iso	406.8 ?	36.5 ?	
Butane-n	426.3 ?	35.7 ?	
Carbon dioxide	304.1	72.9	0.460
Carbon monoxide	134.4	34.6	0.311
Chlorine	417	76	0.573
Cyanogen	401.4	59.7	
Ethane	305.2	48.8	0.21
Ethyl chloride	456 ?	54 ?	
Ethylene	282.6	50.7	
Helium	5.20	2.26	0.066
Hydrogen	33.18	12.8	0.0310
Hydrogen bromide	363.5 ?		
Hydrogen chloride	324.5	83 ?	
Hydrogen iodide	423.9 ?		
Hydrogen sulphide	373.5	89	
Krypton	210.6 ?	54.3 ?	
Methane	190.6	45.7	0.162
Methyl chloride	416.2	65.9	0.37 ?
Neon	44.7	26.9	
Nitric oxide	180 ?	71 ?	
Nitrogen	126.0	33.5	0.3110
Nitrous oxide	309.6	71.7	0.45 ?
Oxygen	154.3	49.7	0.430
Ozone	268 ?	92.3 ?	
Phosgene	456±0.5 ?		
Propane	368.7	45	
Propylene	364.5 ?	45.3 ?	
Sulphur dioxide	430.3	77.7	0.52 ?
Xenon	289.7	58.2	1.155

[a] The absolute zero is taken as 273.1°C.
[b] "Plait point".
[c] "Critical point of contact".

Of the two recent determinations of the critical pressure, preference is given to that of Cardoso and Bell, because their description shows that the work was carefully carried out while Briner does not discuss his apparatus or method.

The only value for the critical density is that of Cailletet and Mathias, which was obtained in 1887 and can not be accepted as very reliable.

Xenon

Date	T_c	P_c	d_c	Obs.
1901	287.9	58.0		1
1912	289.7	58.2	1.155	2
Selected values	289.7	58.2	1.155	

1. Ramsay and Travers: Trans. Roy. Soc. London. 197 A, 71 (1901)
2. Patterson, Cripps, and Whytlaw-Gray: Proc. Roy. Soc. London. 86 A, 579(1912)

Ramsay and Travers make no claim for a high degrre of accuracy in their determinations of the critical constants of xenon because they had only 3 cc of gas, giving 0.006 cc of liquid, and were therefore unable to get complete purification.

From Ramsay and Moore, Patterson and his co-workers procured 120 cc impure xenon. After solidifying the gas and pumping off the non-condensible gases, they boiled away the solid xenon and took the last 20 cc for their measurements. The temperatures were maintained constant to 0.02°. They noted that apparently unless certain precautions were taken xenon and oxygen would physically associate, and later dissociate giving off oxygen which would lower the critical density.

THE STARCH-IODINE REACTION

BY N. R. DHAR

Two distinct views have been put forward in order to explain the mechanism of the starch iodine reaction. Several authors, notably Rouvier[1], Euler and Myrbäck[2] and others have formulated the view that on the addition of iodine to starch paste, definite chemical compounds are formed. The number of formulae denoting the compound starch-iodine has come up to thirteen, the iodine content varying from 3 to more than 20 per cent.

In opposition to the above view, Küster[3] has shown that the blue colour of starch iodide can be easily explained by the phenomenon of the adsorption of iodine by starch. Padoa and Savare[4], Katayama[5], Berczeller[6], Bancroft[7] and Lottermoser[8] are supporters of the adsorption view.

It is well known that starch forms a colloid when mixed with warm water and on the addition of iodine to this colloidal starch the well known blue substance which is certainly colloidal in nature is obtained. It appears that colloidal starch is negatively charged and on the addition of iodine the amount of charge on each particle is increased. Like most colloidal substance starch has a good adsorptive power, as has been shown by Robison[9], Lloyd[10], Rakovski[11] and others. Evidently there is hardly any doubt that adsorption plays a very important part in the formation of the blue substance.

It is apparent that the blue substance, starch iodide, is colloidal in its nature. In order to throw light on the nature and on the constitution of the blue substance, electric conductivity measurements were carried on. Several years ago Duclaux[12], found positively charged ferric hydroxide sol is fairly conducting. In a recent paper Wintgren[13] has determined the conductivity of stannic acid peptised by alkali. Very recently Sen, Ganguly and Dhar have found that negatively charged ferric hydroxide sol is also fairly conducting.

Fifteen grams of Lintners' soluble starch (British Drug Houses Ltd: London) were made up to 1000 cc. using warm water at the beginning. The conductivity of this colloidal solution was determined. When N/10 alcoholic solution of iodine, the conductivity of which was determined before, was added to the starch solution, it was found that the conductivity of the blue

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[1] Compt. rend. **117**, 461.
[2] Ann. **428**, 1 (1922); Arkiv. Kem. Min. Geol. **8**, No. 9, 1 (1922).
[3] Ann. **283**, 364 (1891).
[4] Atti, R. Accad. Lincei, **14**, 1, 467 (1905).
[5] Z. anorg. Chem. **56**, 209 (1907).
[6] Biochem. Z. **84**, 106 (1917).
[7] "Applied Colloid Chemistry", 104 (1921).
[8] Z. angew. Chem. **34**, 427 (1921).
[9] Proc. Camb. Phil. Soc. **15**, 548 (1910).
[10] J. Am. Chem. Soc. **33**, 1213 (1911).
[11] J. Russ. Phys. Chem. Soc. **45**, 7, 13 (1913); **46**, 24 (1914).
[12] Compt. rend. **140**, 1468 (1905); Kolloid-Z. **3**, 126 (1908).
[13] Z. Phys. Chem. **103**, 238 (1922).

substance thus obtained is greater than the sum of the conductivities of the two substances. The conductivity measurements were carried out at 25° and the following results were obtained:—

TABLE I

Substance	*Conductivity*
Absolute alcohol	4.86×10^{-6}
N/10 alcoholic iodine	1.36×10^{-6}
∴N/10 iodine (in alcohol)	8.76×10^{-6}
Aqueous iodine (about N/1000)	4.32×10^{-6}
Water	3.37×10^{-6}
∴Iodine (in water)	0.95×10^{-6}
Starch (colloidal) 15 grams per litre	2.7×10^{-5}
Starch (alone)	2.36×10^{-5}
20cc. starch + .1 cc N/10 alcoholic iodine	2.55×10^{-5}
" " + .2 cc " " "	2.63×10^{-5}
" " + .3 cc " " "	2.74×10^{-5}
" " + .4 cc " " "	3.01×10^{-5}
" " + .5 cc " " "	3.85×10^{-5}
" " + .6 cc " " "	3.93×10^{-5}
" " + .8 cc " " "	4.85×10^{-5}
" " + .9 cc " " "	5.96×10^{-5}

TABLE II

Substance	*Conductivity*
20 cc. starch sol + 1 cc N/10 alcoholic iodine	7.74×10^{-5}
" " " + 2 cc " " "	10.01×10^{-5}
" " " + 3 cc " " "	9.52×10^{-5}
" " " + 4 cc " " "	8.86×10^{-5}
" " " + 5 cc " " "	8.28×10^{-5}
" " " + 6 cc " " "	7.63×10^{-5}
" " " + 7 cc " " "	7.15×10^{-5}
" " " + 8 cc " " "	6.77×10^{-5}

TABLE III

20 cc starch sol + 1 cc alcohol	2.28×10^{-5}
" " " + 2 cc "	1.99×10^{-5}
" " " + 3 cc "	1.83×10^{-5}
" " " + 4 cc "	1.66×10^{-5}
" " " + 5 cc "	1.51×10^{-5}
" " " + 6 cc "	1.39×10^{-5}
" " " + 7 cc "	1.28×10^{-5}

From the foregoing experimental results it is quite clear that on addition of alcoholic iodine to a sol of starch, the conductivity is greatly increased. It will be seen from Tables I and II that, as the amount of iodine goes on increasing the conductivity of the mixture also goes on increasing to a maximum and then it falls off on further addition of iodine. This decrease in the conductivity is certainly due to the falling off of the conductivity of starch on the addition of absolute alcohol. The experimental results in Tables I and III conclusively prove that on addition of absolute alcohol to starch, the conductivity gradually falls off as we go on adding more of alcohol to a definite volume of the starch sol.

On comparing Tables II and III we find that the ratios of conductivities when corresponding amounts of the substances are added are 3.4, 5, 5.2, 5.35, 5.45, 5.5, 5.6 and 5.8. These numbers are in increasing order of magnitude. In other words, these ratios conclusively prove that the greater the amount of iodine added to a definite volume of starch sol, the greater is the conductivity of the mixture. Consequently, the foregoing experimental results prove that on the addition of alcoholic iodine to starch, the conductivity of the blue substance produced is much greater than the sum of the conductivities of the reacting substances (viz starch and iodine) It seems,therefore, that the blue compound is appreciably conducting and gives out some ions probably of the micellar type. From my conductivity experiments I am of the opinion that this blue substance formed by the adsorption of iodine by starch is something like an unstable chemical compound and behaves like an unstable iodide.

In order to explain the conductivity of colloids and substances like soap, the micelle theory of ions has been advanced.[1] The same conception of ionic micelle has been applied to a sol of stannic acid peptised by alkali[2]. It is supposed by these authors that one of the ions given out by colloids and substances like soap, which is micellar in nature, contains many atoms and is very heavy[3]. It seems, probable, that with starch iodide we get a heavy micellar ion containing starch and the other ion may be the simple iodide ion.

In order to see whether other colloids would show greater conductivity as in the case of starch iodide several conductivity experiments were made with weak electrolytes like acetic acid, boric acid, arsenious acid, etc., when treated with freshly precipitated and well washed ferric hydroxide. Starting with a sample of glacial acetic acid which is 16.5 N. I find it is practically non-conducting. When freshly precipitated and well washed ferric hydroxide, which is dried in air, is added to glacial acetic acid and shaken the conductivity of the mixture is highly increased. Similarly the conductivity of 13.75 N acetic acid in presence of freshly precipitated ferric hydroxide is greatly increased. But with more dilute acetic acid the reverse is the case. Thus with 2.38 N acetic acid the conductivity is decreased on the addition of ferric hydroxide. It is well known that a positively charged ferric hydroxide sol is obtained by shaking freshly precipitated ferric hydroxide with dilute acetic acid. The whole of the colloid can be readily coagulated by the addition of electrolytes like $(NH_4)_2SO_4$, Na_2SO_4 etc. In this case practically the whole of the iron remains as a colloid and not as ferric acetate. The decrease in the conductivity of dilute acetic acid on the addition of ferric hydroxide is certainly due to the adsorption of acetic acid by ferric hydroxide and hence the concentration of the acid is decreased.

In a foregoing paper from this laboratory it has been shown that by shaking freshly precipitated ferric hydroxide with arsenious acid a negatively

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[1] See Zsigmondy: "Chemistry of Colloids", 166 (1917); Pauli and Matula: Kolloid-Z. 21, 49 (1917).

[2] Wintgren: loc. cit.

[3] Compare Dhar: Z. anorg. Chem. 1913, 80, 43 (1913).

charged sol of ferric hydroxide is obtained. The decrease in the conductivity of arsenious acid on the addition of ferric hydroxide is also certainly due to the adsorption of arsenious acid by ferric hydroxide, which is a good adsorbent of arsenious acid. Exactly similar results are obtained with boric acid. With concentrated acetic acid the case is different. If ferric hydroxide is added to glacial or very concentrated acetic acid the conductivity is enormously increased due certainly to the formation of the electrolyte ferric acetate. That ferric acetate and not colloidal ferric hydroxide is formed is shown by the fact that no coagulation takes place on the addition of electrolytes to these solutions. In these cases the formation of the conducting electrolyte ferric acetate more than counteracts the adsorption of acetic acid by ferric hydroxide and hence the conductivity is greatly increased. Hence the formation of ferric acetate or colloidal ferric hydroxide on the treatment of acetic acid with freshly precipitated ferric hydroxide depends on the concentration of acetic acid and this is guided by the following mass action equilibrium

$$Fe(OH)_3+3CH_3\,COOH = Fe(C\,H_3COO)_3+3H_2O$$

Looking at the whole problem it seems that the blue substance obtained by the adsorption of iodine by starch is something like an unstable chemical compound which can give off ionic micelle in water.

It will be interesting to find out whether there is any change in the conductivity of the reacting substances (viz. sulphur dissolved in $S_2\,Cl_2$ or CCl_4 or CS_2 and the raw caoutchouc). That there is some chemical action in the process of vulcanisation will be evident from the fact that its temperature coefficient for a 10° rise is 1.8. This value is greater than the average temperature coefficient of homogeneous reactions.[1] In our experiments on the adsorption of electrolytes by manganese dioxide no effect of temperature on the phenomenon of adsorption was observed.

The blue colour of starch iodide is readily destroyed by chlorine, silver nitrate, mercuric chloride, iodic acid and other oxidising agents, like nitric acid, chromic acid, etc. This fact can be easily explained on the view that the blue substance is an unstable iodide. The following results were obtained in the decolourisation of the blue substance with mercuric chloride:—

10.cc of the starch solution with different volumes of iodine solution titrated against M/5 $HgCl_2$ Solutions.

Volume of N/10 iodine Solution.	Vol. of M/5 $HgCl_2$ Sol.
0.5 cc	2.2 cc
1 cc	8.4 cc
1 cc	8.4 cc
2 cc	16.5 cc
3.cc	24.7 cc

In order to decolourise with nitric acid far greater quantity of the oxidising agent is necessary.

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[1] Compare Dhar: Proc. K. Akad. Weten. Amsterdam, 21, 1042 (1919).

10 cc starch and 0.5 cc of alcoholic iodine require 110 cc of 3.75 N HNO_3.

There has been a great deal of controversy as to whether iodide ions are necessary in the generation of the blue substance. In Mylius' formula of starch iodide, HI is regarded as a part of the blue iodide of starch. This view has been corroborated by Roberts[1], Lonnes[2], Hale[3] and Sen[4]; while Rouvier[5], Meineke[6], Berczeller[7], Euler and Myrbäck[8] have shown that potassium iodide is not necessary for the production of the blue substance. Lottermoser (loc. cit.) appears to have taken an intermediate position and believes that iodides are required temporarily for the production of the blue colour. I have observed that on the addition of a freshly prepared alcoholic solution of iodine to starch paste or colloidal starch the blue colour immediately appears. In this case iodine did not get time to undergo hydrolysis according to the equation $3I_2+3\ H_2O=5HI+HIO_3$, hypoiodous acid being formed as an intermediate product. The hydrolysis of iodine being a non-ionic change is expected to be slow; hence the immediate appearance of blue colour on the addition of alcoholic iodine to colloidal starch does not support the view that iodide ions or HI are necessary for the production of the blue colour, because at the beginning there is hardly any HI in the mixture. Of course, according to the conception advanced in this paper the blue substance itself is an unstable iodide, which gives off iodide ions in solution.

The great amount of HNO_3 necessary for the discharge of the blue colour seems to be against the view that HI is necessary for the formation of the blue colour.

The effect of several electrolytes on blue starch iodide has also been investigated. In this line of research there has been a considerable difference of opinion amongst previous investigators. Standard solutions of KCl, $(NO_3)_2$, Ba K_2SO_4, KI, $Al_2(SO_4)$, KBr and $BaCl_2$ were prepared and in clean test tubes 5cc of each of the solutions added to 10 cc of the starch iodide obtained by mixing 100 cc of starch (15 grams per litre) with .2 or .3 or .4 or .5 cc N/10 alcoholic iodine. In all cases 5 cc of water was added instead of the electrolyte to 10 cc of starch iodide and this tube served as the blank one for comparison with other tubes.

The effect of electrolyte on starch iodide seems to be complicated specially that of KI, which markedly intensifies the blue colour.

With other electrolytes the general effect seems to be coagulating in its nature. On the addition of the electrolyte the particles of the colloidal starch iodide coalesce with one another and become larger and hence the blue colour

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[1] Am. J. Sci. (3), **47**, 422.

[2] Z. anal. Chem. **35**, 409.

[3] Am. Chem. J. **28**, 438 (1902).

[4] Proc. K. Akad. Wet. Amsterdam (1923).

[5] Compt. rend. **114**, 749.

[6] Chem. Z. **18**, 157 (1894).

[7] Loc. cit.

[8] Loc. cit.

[9] Compare Bray: J. Am. Chem. Soc. **32**, 932 (1910).

is intensified though to a varying extent depending on the nature rather than the valency of the ions in question. It will be interesting to investigate whether the coagulation of blue starch iodide follow the Schulze-Hardy rule.

Summary

(1) When alcoholic iodine is added to starch sol, the conductivity of the substance formed is much greater than the sum of the conductivities of the individual substances.

(2) The substance obtained by the adsorption of iodine by starch is appreciably conducting and behaves something like an unstable iodide. It seems probable that micellar ions are given out in sol.

(3) It seems probable that the presence of outside iodide ions is not necessary for the formation of the blue substance. The hydrolysis of iodine is a slow process.

(4) Electrolytes have the general effect of intensifying the blue colour by the coalescence of the smaller particles into bigger ions caused by thier coagulating effects.

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THE RECOGNITION OF BLUE[1]

BY WILDER D. BANCROFT

Matthews[2] says that "there is a peculiar variety of peeler cotton known as 'blue bender' cotton. This fibre is characterized by a bluish color which cannot be bleached out by the usual methods employed for the bleaching of ordinary cotton. It receives its name from occurring in the 'bends' of the Mississippi River valley. The exact nature of the color and the cause of its formation in this variety of cotton are not known. By some it is supposed that the defect arises from the plant being touched by frost too early, while others assume that the cause is to be found in some ingredient in the soil. Outside of its defective color and resistance to bleaching, the appearance and quality of the fibre are otherwise unimpaired."

We were, of course, interested in this mysterious blue, and, through the courtesy of the appropriate Government Bureau in Washington, we received a good-sized sample of this 'blue' cotton. Unfortunately nobody in the Department of Chemistry at Cornell was able to see any blue in the specimen and consequently we were unable to account for what was to us an invisible color. The cotton was not yellowish like ordinary raw cotton and was a grayish-white to our eyes. If one harks back to what one knows about washing, one might assume that the yellowish cotton had been turned grayish white by the addition of a blue pigment and that in that sense it was a 'blue' cotton. One could equally as well assume that the yellow had never been developed, and this would eliminate the hypothetical blue. A letter to Washington asking how we should look at the cotton in order to see the blue was treated with the silent scorn which perhaps it deserved. An appeal to Dr. Matthews was not helpful because he said that he could see blue in nearly everything, including graham crackers.

The whole matter of the recognizing of blue is very much in the air. Rivers[3] has some definite views on the color vision of primitive races which are interesting, even though they have not been accepted generally. Speaking of the Murray Islanders and their ability to name colors, he says, p.55, that "it will be seen that there was great definiteness and unanimity on the nomenclature for red, rather less so for orange and yellow, less so for green, and very great indefiniteness for blue and violet. Soskepusoskep was evidently the most definite word for green, while the word used most frequently for blue and indigo was bulubulu, which was the English word reduplicated and with

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[1] This paper is a necessary consequence of experiments supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] "Textile Fibres," 264 (1913).

[3] Reports of the Cambridge Anthropological Expedition to Torres Straits, 2, 48 (1901).

the contiguous consonants separated [no reference to Yale]. The old men agreed that their own proper word for blue was golegole (black), and they regarded it as quite natural to apply this name to the brilliant blue of the sky and sea."

"Of the four well-established and definite colour names of the Western Tribe, it will be seen that three have the same derivation as in Murray Island. In both tribes the common name for red is derived from blood, and the most usual name for green from bile, while names for yellow are derived from ochre, though in Murray Island there was a tendency to name blues and greens after the sea (karemgausgaus, sea-green, and karemgolegole, sea-black), and in the Western Tribe a definite name for these colours derived from the word for sea has become established. It is noteworthy that the sea, rather than the sky, should have been the source of the word for blue," p. 62.

"On comparing the three colour vocabularies of Torres Straits and the Fly River district, it will be seen that they resemble each other closely in that in each the words for red and yellow are far more definite and well established than those for other colours. In each there is also a word which is especially used for green, poroporo in Kiwai, soskepusoskep in Murray Island, and ildegamulnga in Mabuiag, but these words are not used with the unanimity which is present in the nomenclature for red and yellow. As regards blue, the three languages may be taken as representatives of three stages in the evolution of a nomenclature for this colour. In Kiwai there is no word for blue; many blues are called names which mean black, dark, dull or dirty, while other blues are called by the same word which is used for green. In Murray Island there is no proper native term used for blue. Some of the natives, especially the older men, use golegole, which means black, but the great majority use a term borrowed from the English and modified so as to resemble the other members of their colour vocabulary. Another word, suserisuseri, is used occasionally for blue and also for green, and in the absence of the borrowed word this might have been used more often.

"The language of the Western Tribe of Torres Straits presents a more developed stage in the existence of a word, maludgamulnga, which is used definitely for blue, but is also used for green. In this language, however, traces of the tendency to confuse blue and black still persist in the use of such words as inuradgamulnga and kubibudadgamulnga to denote blue.

"In dealing with Australian languages later, we shall meet with instances of a degree of development of colour nomenclature still less developed than that of Kiwai in which only red, black and white seem to have definite, established names.

"There are many other languages in stages of development comparable with those of Kiwai, Murray Island and Mabuiag. The confusion of blue and black is very common. It has been noted in Melanesian language by Strauch (New Hanover and New Britain) and by Schellong (Malayta in the Solomon Islands), and I found a distinct tendency to confuse black and blue in nomenclature among natives of Tanna and Lifu (see p. 85). According to Magnus, the same confusion is found among the Bushman and Ovaherero of South Africa, the Hovas and Madagascar, the tribes of the Nilgiri Hills in India and the natives of Borneo. Andree quotes the same confusion as occurring among the Mpongwe of the Gaboon and the Caribs of South America. Keller found that ninety percent of the Nubians of the hills called both blue and black 'hadel,' while those of Suakin gave each a different name. The Nubians examined in Germany by Virchow and others also called both blue and black, 'hadel'. Almquist found that the Chukchis gave the same name to dark blue as to black and Gibbs gives the same peculiarity in the Chinook language, light blue having a different name. The modern Egyptian peasant also uses the same words for black and dark blue.

"There are other races who resemble the inhabitants of Murray Island in having borrowed a word for blue from another language. The English has been borrowed by many African races, often taking the form of 'bru.' The Maoris use the English word changed into 'puru.' The Battas of Sumatra use the word 'balau,' borrowed in a slightly modified form from the Dutch. They are also said to have borrowed the word 'biru' from the Malays, but this is probably a modification of the English word. Some races in Borneo are said to use a word 'hidjan' borrowed from the Malay, and the Berbers are said to use a word 'samawi' (sky color) borrowed from Arabic. The Hindustani word 'nil' is used for green and blue by several Asiatic peoples including the Tamils and Siamese.

"The Samoyeds sometimes use the Russian word 'sjinioi' for blue. In the Philippine Islands the words used for green and blue by several tribes, such as the Ilocos, Tagals, and Bisayos, have been borrowed from the Spanish, and one of the Araucans of South America examined by Kirchhoff also called blue 'azul.'

"The use of the same word for green and blue is very common. Many instances are given by Andree and Magnus in the papers already cited, and many other instances could be added. It will perhaps be sufficient to mention that one instance occurs so near home as in the Welsh language, in which there is only one word 'glas' for both green and blue.

"In some languages one finds a word used for both green and blue, and in addition, other words by which these colours may be distinguished. In Mabuiag the case was somewhat different. In this Island there were two words, each used for both green and blue, but it seemed as if these words were in process of becoming terms by means of which the two colours could be distinguished.

"Another feature which was common to the three languages of Torres Straits and the Fly River was the absence of a word for brown. Brown papers and wools were called red, yellow, grey or black, according to their colour tone and shade. In Mabuiag names were given to special browns, but it was quite certain that there were not generic terms for brown in the sense in which we use the word. When a number of wools were put together which the European would call brown, the natives would not acknowledge that any one term would apply to all or even to any considerable group of them.

"The absence of a word for brown appears to be characteristic of very many languages, probably of the great majority of the languages of the world. Among those which I have had opportunity of investigating, I have found no word for brown in several Australian, Melanesian and Polynesian languages, in Tamil, Eskimo, Welsh and the Arabic of the Egyptian peasant. The absence of a word for brown has been noted in many other races. Bastian notes that the Siamese call brown 'dam-deng,' meaning 'black-red.' Kotelmann found that the Lapps called brown 'tscharpis roksad,' again meaning 'black-red'. The Ainus call brown 'furiambe', red being 'fure'. Pergens found that of the fifty-seven Congolese examined by him, only two could give a word for brown; one called it 'moïndo', which was also used for black, and the other 'ossingaiumbayéta,' m'bayéta being used for pink. Gatschet records that a word for brown is absent from several American Indian (Amerind) languages, while in others there may be several terms for this colour. It is possible that, in the latter case the words used were names for special browns, as in Mabuiag, and were not true generic terms for brown. This may also be the case in other languages, such as Patagonian, Tomgan and Araucan, in which names for brown have been recorded.

"The records given of the colour names of several parties of Nubians traveling in Germany show how easily mistakes may be made in such a matter. Kirchhoff concluded that 'hamasch' was a definite word for brown, while the same and other Nubians examined by Nachtigal and Cohn gave hamisch or hamasch as a word for grey and for dark and impure colours generally, while it was also used for violet.

"Schellong gives 'mela' as a word for brown in two Melanesian languages. This is probably the same word as mera, which is a common Melanesian term for 'red'.

"The confusion of brown and violet is common. It will be remembered that both occasionally received the same names in Murray Island and in Mabuiag. Gatschet notes that the Kalapuya Indians of north-west Oregon call violet 'tútĕlu' and brown 'púdschnank tútĕlu,' meaning "not quite violet." The Greeks use oktsadi both for violet and dark brown. Kirchhoff notes that the same confusion is still common in German villages, and that when Halle students wearing violet caps are seen, the villagers say "Here come the browns." Kirchhoff also notes that the middle High German 'brün' was used for violet.

"There appears to have been no word in Homeric Greek which one can regard as equivalent to brown, and I am indebted to a note from the Rev. H. T. F. Duckworth that the same is true of the Greek spoken by the majority of the inhabitants of Cyprus at the present day. They call dark brown objects *μαῦρος*, which is the word in common use for black, while other brown objects are called *κόκκινος*, which is also applied to brilliant scarlet," pp. 66-69.

"The observations so far described show that in spite of the absence or indefiniteness of terms for blue, this colour can be recognized by the Torres Straits islander, while different shades or tints of blue can be distinguished from one another, and the same is true of other races in which the same defect of colour nomenclature exists. It is, nevertheless, possible that there may be some degree of insensitiveness to this colour which makes a given blue a darker and a duller colour than it is to European vision, and may help to account for the confusion of this colour with black," p. 70.

"The observations on direct vision, rough though they were, brought out one point beyond all doubt which appears to be in conflict with the other observations made with the tintometer and coloured wools. There was no doubt that the colour blue was recognized readily, even more readily than other colours. The colour of the patch used was saturated, but if the colour had been relatively dark to the peripheral retina of these people, one would certainly have expected the size of the field to be diminished. Schöler's more exact observations also show that in another race, presenting much the same defect of nomenclature for blue as existed in Torres Straits, blue was readily recognized in indirect vision, its limit being outside that for red.

"The most ready way of reconciling the two sets of observations is to suppose that the defective sensibility to blue is due chiefly, or altogether, to the influence of the macula lutea. It is well known that owing to the yellow-red pigmentation of the region of direct vision, blue and green rays are absorbed more strongly than in the extra-macular regions of the retina. On this account blue is a less intense colour to the macular region of the normal eye than it is to the extra-macular region.

"There is, so far as I know, no actual evidence that the yellow pigmentation of the macula is greater in black-skinned than in the Caucasian races, but there is very little doubt that this must be the case. If so, the absorption of green and blue rays would be greater than in the European eye and may account for the relative insensitiveness to blue.

"The patch of colour shown in the tintometer was 13 mm. in diameter at a distance of 32 cm from the eye, i.e. with steady and direct fixation, the image of the patch would fall wholly within the macular region. During movements of the eye and when looking at the adjoining patch, the extra-macular regions of the retina would be stimulated, but the influence of the macular pigment in direct fixation would probably be of most importance.

"If this view is correct the defective sensitiveness for blue is to be regarded as a function of the pigmentation rather than of the primitiveness of the Papuan visual organ. It is interesting in this connection that when Virchow was examining natives in Berlin in 1878, he found that the difficulties in naming blue and green became very much less if he used large sheets of coloured paper instead of small patches," p. 79.

"I cannot guarantee the accuracy of these vocabularies (Queensland) as I can those of Torres Straits languages, but I think there can be no doubt as to the main features of the colour terminology of these tribes. In all cases there were definite words for black, white and red, the word for red being used also for purple, and in some cases for orange. The Fitzroy natives seemed to differ from those of Seven Rivers in that a fairly definite name for yellow and green had also been evolved. Blue and violet were by nearly all given the same name as black. There appeared to be no trace of a word for brown.

"These main features appear to be generally characteristic of Australian languages. Kirchhoff found that some natives of the Frazer River in Queensland had definite names only for white, black and red, the word for black being used for blue and dark colours in general. In addition to these definite colour names, Kirchhoff obtained as many as seventy names, which were almost certainly of the same kind as those used in Mabuiag, and it is possible that with more complete investigation I should have found the same with my natives. In the Middle Burnett district in Queensland, Semon only gives names for black, white and coloured. Roth states that the natives of North-West Central Queensland have definite names for red and yellow, and that blue is very often confounded with black, so far as nomenclature is concerned. It is perhaps worth noticing that in the comparative vocabulary given by Matthews in *Eaglehawk and Crow*, only the words for red, white and black are included.

"The Australian languages present a lower stage of evolution than was found in Torres Straits. In what one may regard as the lowest of the three Papuan languages, viz. that of Kiwai, there were certainly definite terms for red and yellow, while green was probably in progress of being distinguished by a special term. The Fitzroy language may seem, so far as my evidence goes, to be one in which a term has come into use for yellow and green, these colours being still classed together, while in the Seven Rivers languages the definite colour vocabulary appears to be limited to three terms. This stage of the evolution of colour language has been found in other parts of the world. The Todas of the Nilgiri Hills are said only to have words for white, black and red. Riis states that the people speaking the Akwapim dialect of the Tshi language in West Africa only have three adjectives for single colours, viz, fufu, white; tuntum, black; and koko, red. They call blue 'bru', obviously a corruption of the English word. According to Buchner, the Bantu have only three words for colours, one for black, which also means blue, one for white, which also means yellow and light, and one for red. Moncelou states that the natives of New Caledonia only have definite terms for black, white and red," pp. 89.

"Although the ordinary form of colour-blindness was absent in Torres Straits, the colour vision of the Papuans and of certain other races examined was certainly not of the same type as that of Europeans. I may here shortly sum up the reasons which have led me to conclude that the colour vision of the Papuan is characterized by a certain degree of insensitiveness to blue (and probably green) as compared with that of Europeans. To start with the defect of language; the races examined by me had either no word for blue or an indefinite one, while their nomenclature for red, and usually that for yellow, was extremely definite. The philological argument is, however, not a very strong one, for the defect of language might depend on many factors of which however, physiological insensitiveness may be one. One cannot, however, wholly ignore the fact that intelligent natives should regard it as perfectly natural to apply the same name to the brilliant blue of sky and sea which they give to the deepest black. I cannot help, too, attaching importance to some of the instances of nomenclature met with in Mabuiag. I have already described how many of the older natives of that island compared every colour to some natural object, apparently showing, as regards most colours, a high degree of appreciation of differences of hue and shade, and yet these natives would deliberately compare a brilliant and saturated blue to the colour of dirty water or to the darkness of a night in which nothing could be seen. Every detail of the behaviour of the natives in connection with the naming of colour was consistent with the idea that blue was to them a darker or a duller colour than it is to us," p. 94.

"There can be very little doubt, however, that any physiological insensitiveness which may exist, can only be one of the factors determining the characteristic features of primitive colour nomenclature. The deficiency which I have found in Torres Straits is only partial, and even if one were to assume that other races would show the same peculiarity, this partial deficiency could not wholly account for the total absence of a word for blue which is a feature of so many languages. To the European eye there is a much closer resemblance between blue and black and between green and black than there is between red and black and yellow and black, and this psychological fact was the basis of the theory of colour put forward by Goethe. The fact that this difference exists, alone goes far to explain the earlier discrimination of red and yellow in primitive language," p. 95.

"Another factor which may have contributed to the causation of the indefinite nomenclature for blue and green is the absence of aesthetic interest in nature on which I have already commented. The blue of the sky, the green and blue of the sea, and the general green colour of vegetation do not appear to interest the savage. It is the individual objects which he can take in his hands and use in his daily life which interest him, and it is to the attributes of these that names are given," p. 96.

Titchener[1] criticizes severely the conclusion of Rivers that the Murray Islanders are insensitive to blue. He believes that the word golegole means uniform, even, or undifferentiated, and not black. He adds that "the absence of a word for blue, if the fact stood alone, is no argument against sensitivity to blue. For the savage names only what interests him, and we have seen that his interest is directed upon the interpretation of sensory stimuli. But there is in Murray Island no such sensory stimulus, no object of daily use or interest —no pigment, for instance—of a blue color. . . . I see no reason why they should be interested in the brilliant blue of sky and sea, for the brilliant blue means fine weather and calm."

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[1] Proc. Am. Phil. Soc. 55, 221-230 (1916).

Among us "blue flowers, blue articles of dress, blue hangings and blue china and other [blue] household gear are common enough; and experiment shows that blue sky and green grass are more often associated than are red and yellow to any object of their color. We live in a world where blue has its acknowledged place. The Murray Islander does not. Blood he knows, and red and yellow ochre, and the brilliant deep-green gall bladder of the turtle—all of them objects of the highest importance in the conduct of his life; but blue he has no dealings with."

It has often been claimed that Homer had no especial word for blue and this usually arouses the wrath of some Greek scholars who believe that this means that the Greeks were color blind or at least were insensitive to blue. This does not follow at all though Gladstone[1] believed that it did. We can accept his evidence without adopting his conclusions. The two possible words for blue are *κυάνεος* and *γλαυκός*. With regard to the first Gladstone points out that there is no one color that can apply in all the cases in which Homer has used the word, p. 465. "The hood of Thetis is closely akin to black; the prow of a ship to at least a dull red; the sand is of russet or a lightish brown; the cloud a leaden grey; the hair and eyebrows are of a deep but not a dull colour; the cornice in the hall of Alcinous must have been in relief and contrast as compared with the copper wall; and sufficiently light or clear to strike the eye at a distance, in an interior lighted at night only from the ground. With perhaps this exception, the word 'dark' will cover the uses of *κυάνεος*; but dark derives its force from a relation to light and not to colour."

In the palace of Alcinous the cornice is believed to be the native, blue carbonate of copper, p. 498, and "in later Greek at least, the word acquired other significations: such as lapis lazuli, the blue cornflower, the rockbird (also being blue), and, lastly, a blue dye or lacquer," p. 496; but the blueness of the copper carbonate was not apparently the point that Homer wished to emphasize.

Homer applies the word *γλαυκιόων* "to the eye of a lion, when, reaching the height of his wrath, he makes his rush at the hunters. The last of these passages seems effectually to fix the sense of the term. The word *γλαυκιόων* describes a progression. The lion does not enhance the colour of his eye as he waxes angry. If, for example, *γλαυκὸς* can be taken as blue, it certainly does not become more blue: on the contrary, rage, when kindling fire in the eye, rather subdues its peculiar tint by flooding it with a vivid light. So the word seems clearly to refer to the brightening flash of the eye under the influence of passion. Of light and its movement, as also of sound and of beautiful form, Homer's conceptions are even more distinct and lively than those of colour are, if not dull, yet at least indeterminate.

"*Γλαυκὸς* is derived from *γλαύσσω*; and has for its root *λάω*, to see. The meaning of bright or flashing will suit the sea as well as the epithet blue. And it suits Minerva far better. 'Blue-eyed' would be for her

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[1] Homer and Homeric Age, 3, 457 (1858).

but a tame epithet. The luminous eye, on the contrary, entirely accords with her character, and belongs to a marked trait of those primitive traditions, which she appears to represent," p. 474.

The general theory has been criticized by Grant Allen,[1] who believes that "the colour sense must be a common property of all mankind, in every country, and in every age."

"Here, however, we are confronted by the adverse theory of Mr. Gladstone and Dr. Hugo Magnus, who endeavour to convince us, on the contrary, that the sense of colour is quite a late and post-historical acquisition of the human race. From philological evidence in the Vedas, in the Hebrew scriptures, and in the Homeric poems, they conclude that some three thousand years ago the foremost tribes of the Semitic and Aryan races were incapable of distinguishing between red, blue, green, and yellow. Starting from such an imaginary primitive state, they trace up the development of the colour-sense through the succeeding ages, marking out four principal stages in the growth of the perception. All this startling theory they set forth on purely philological grounds. I shall give briefly the main points of their hypothesis, almost in the very words of Mr. Gladstone.

"The starting-point is an absolute blindness to colour in the primitive man. Thence, in the progressive education of the organ, three chief colours have been successively disclosed to it, and have appeared in the order of their greater or less refrangibility—red, green, violet. The first stage attained is that at which the eye becomes able to distinguish between red and black. Red comes first into our perceptions, because it is the most luminous of the colours; but, says Geiger, in the Rigveda white and red are hardly severed. In the next stage of the development, the sense of colour becomes completely distinct from the sense of light. Both red and yellow with their shades (including orange) are now clearly discerned. To this stage Magnus refers the Homeric poems, in which red and yellow colours are set forth, while no mention is made (according to these authorities) of green or blue. The characteristic of the third stage is the recognition of colours which in point of luminousness belong to neither extreme, but are in a mean, namely, green with its varieties. Finally, in the fourth stage of the development, we find an acquaintance with blue begins to emerge. This is a stage not even now reached universally; for example, in Burma (it is alleged by Bastian) a striking confusion between blue and green is a perfectly common phenomenon, and a like confusion is not unusual among ourselves by candle light.

Of course, the first point which strikes an evolutionist on being confronted with this elaborate theory is the utter inadequacy of the time assigned for the origin of such strong and fundamentally differentiated sensations as those of colour. Had Dr. Magnus said three million, or even thirty million years, the evolutionist could have hesitated on the score of insufficient elbow-room; but when our author suggests three thousand years for the growth of a radi-

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[1] The "Colour-Sense," 202, 207, 212, 218, 254 (1892).

cally separate set of sentient organs, our incredulity becomes absolute and irrevocable. It would be useless, however, to oppose the doctrine on such purely *a priori* grounds, only efficient for those who accept the general hypothesis of evolution; and we must therefore seek to discover what *a posteriori* arguments can be urged on the other side, against the philological evidence of Mr. Gladstone and Dr. Magnus.

"There are two kinds of proof for the universality of the colour-sense in man which we may offer in opposition. The first method consists in showing that all human races at the present day, including the lowest savages, do actually possess just the same sense of colour as ourselves: whence we may argue with considerable probability that they derive that sense from a common ancestor, and that the Homeric Akhaians were not likely to be destitute of perceptions possessed by the Bushmen, the Australians, and the hill-tribes of India. The second method consists in showing that works of art and other remains of the early historical races of pre-historic man yield evidence that the colour-sense was fully developed long before the epoch of the Iliad or the Book of Genesis. Both these methods of proof we shall employ here."

The Ojibways "can distinguish clearly between blue and green, and also between blue and violet, though they have no distinctive name for the latter colour. They have, however, no less than seven different colour-names, including separate words for green and blue. Other correspondents mention like facts of other tribes. In all, the power of discrimination seems quite equal to our own, though the nomenclature generally extends only to four or five most markedly different colours."

"As regards the Malay archipelago generally, Mr. Wallace's vocabularies contain words for black, white, red, and blue in thirty-three Malayan languages. Mr. W. Gifford Palgrave mentions white, yellow, red, green, and blue among the dyes used by the Philippine Islanders. . . . I may add that whenever I have had the opportunity of consulting intelligent travellers upon this subject, they have always at once given their opinion that the savages with whom they were conversant distinguished all colours perfectly. . . .

"Such are a few selected instances from the mass of evidence which might be adduced in favour of the belief that all existing races possess a fully-developed colour-sense. I think they will probably suffice to show the general truth of our proposition. If savages so low as some of these actually enjoy such high powers of discrimination, can we consistently deny the like to the early Hebrews and Akhaians? I have not so high an opinion as Mr. Gladstone of the rude Homeric warriors or the fierce conquerors of Lower Syria, but at least I cannot believe that they were less advanced in simple sensuous perceptions than the naked Todas or the wild half-human Andamanese.

"Now let us go on to inquire whether we cannot find abundant proofs of a highly evolved colour-sense long before the period to which the criticisms of Geiger and Magnus refer. . . . An inspection of the existing remains in the Louvre and the British Museum will sufficiently prove to the most sceptical that the colour-sense of the Assyrians was essentially identical with our own.

. . . A few hours spent at the British Museum, especially amongst the mummy-cases will do more to convince the reader of the Egyptian colour-sense than pages of quotation."

"We may rest content with the cases of the Egyptians and the modern savages, having the post-historical theory here on the horns of a dilemma which it cannot easily escape. If, on the one hand, we put forward only the case of Egypt, it might be answered that the development of a colour-sense is a question of relative culture, not of mere chronological order; and if, on the other hand, we put forward only the case of modern savages, it might be answered that the development of a colour-sense is a question of chronological order, not of relative culture; but if we put forward the two cases together, it will hardly be possible for any one to shirk the first difficulty by answering us in one way, and then to shirk the second difficulty by answering us in the other.

"When we examine the extraneous arguments by which the theory is supported, we find that they have very little real weight. Thus it has been suggested that colour-blindness may be a survival from this earliest type of vision; but when we look a little deeper into the question we recollect that the commonest form of colour-blindness is that which cannot discriminate red from green—whereas red ought, according to the theory, to be the most universally discriminable of all—while it is yet quite able to discriminate green from blue. Furthermore, there is a good reason for believing that colour blindness is far commoner in civilised communities than amongst savage tribes. According to M. Favre, no less than 3,000,000 persons in France are afflicted with this defect, while Stilling places the proportion in Western Europe generally at five percent. On the other hand, the abnormality appears to be infrequent or unknown amongst the lower races; so that it must be regarded rather as a disease of civilisation than as a survival from the primitive state."

"Primitive man in his very earliest stage will have no colour terms whatsoever. He will speak of concrete objects only, and when he uses their names he will use them as implying all their attributes. He does not need to say *red blood*, for all blood is red; nor *green leaves*, for all leaves are green. *Blood* and *leaf* by themselves are quite sufficient for every one of his simple purposes.

"But when a man comes to employ a pigment, the name of the pigment will easily glide into an adjectival sense. The earliest colour terms will thus be produced. I learn from Mr. Whitmee that the Samoans use three kinds of pigment— a red volcanic earth, a molluscan purple, and a turmeric; and the names of these three pigments are applied as colour terms. So, too, many other informants have given me like instances with other races. A large proportion of our own colour terms are derived from dyes or pigments. Such as *crimson* (or *cramoisi*) from the Arabic *karmesi*, the kermes; *vermilion* or *vermeil*, from *vermiculus*, because it was supposed to be the product of a worm; *gamboge*, from Cambodia, the place of its export; *indigo*, from Spanish *indico*, the Indian dye; and *saffron*, from the common English plant.

"Moreover, we saw that red is the earliest colour used in decoration, and accordingly it is the earliest colour which receives a special name. This fact has been fully brought out by the researches of Geiger, Magnus, and Mr. Gladstone; and it will not therefore be necessary to accumulate further proofs in the present volume. The early prominence of red, however, has left some curious traces in language, as well as in art, to the present day, which deserve a passing notice here. Thus the Indo-European dialects contain a number of words for this colour from a common root—*e-ruth-ros, rubeus, russus, ruadh, roth, red, rouge, robbio, roux, ruddy*, etc.; while there is no such widespread and common root for blue—*caeruleus, blau, azul*—nor for green—*chlöros, viridis, grün*. Again, we English have a great number of subordinate colour terms in popular use to express the various shades of red, such as *crimson, scarlet, vermilion, rosy*, and *pink*, besides less definite words like *cherry, ruddy, russet, carnation, blushing, sanguine*, or *ensanguined, ruby*, and *roseate*; but we have few or no words to express the shades of green, while physicists have had to introduce the conventional terms indigo and violet to designate the widely different but unnamed hues which result from the quickest light-waves. Once more, while the nouns of brightness and its opposite give us the verbs *to lighten* and *to darken, to whiten* and *to blacken*, and while the primitive art-colour, red, gives us the verb *to redden*, we have no such words in our language as *to bluen* and *to greenen*. And it is a significant fact, as regards the aesthetic position of green, that whereas the use of 'blue' in laundries has given rise to a technical verb of washerwoman, *to blue*, we have absolutely no verb meaning *to green* or *to verdigris*. Finally, the mixed colours, orange and purple, into which red enters as an element, have separate popular names, but no other mixed colours have any but technical designations; and while these red-like words, with yellow, the adjunct of red, yield us the verbs *to purple, to crimson, to encarnadine*, to *ensaffron*, and so forth, I cannot call to mind a single similar expression with reference to the less refrangible rays.

"During the period or stage in which red forms the main or only decorative colour, red alone has a conventional or abstract name. All other hues are spoken of by comparison with well-known objects. It is not the habit of the early mind to refer to the sky as *blue*, or the leaves as *green*; on the contrary, it speaks of blue things as "sky-faced" (*caeruleus*), and of green things as "sprout-like" (*viridis*, connected with *virere*; *grün, green*, connected with *grow*). The primitive man would no more think of saying that the sky was sky-faced, or the leaves leaf-like, than we should think of talking about an orange orange, or a lilac lilac.

"But so soon as the blue becomes a recognized art-colour, either through the use of pigments or of decorative jewels, a name for blue springs up. One of the commonest in Europe is that of *azure, azur*, or *azul*, derived from the Persian *lâzur*, lapis lazuli. We have already seen that this stone was very early imported from the east, and it was natural that it should give a name to the hue in question, because it was largely employed for artistic purposes. *Emerald* and *turquoise* are similarly used at the present day to designate various shades of green.

"At this second or red-blue stage, the word for blue seems often to be applied also to green. This is not surprising when we recollect how very little difference really exists between these two colours. Indeed, I am convinced that we only have separate names for them at all because the commonest green in nature, that of foliage, and the commonest blue in nature, that of the seldom-seen open sky, are so very wide-spread and so much more strikingly different from one another than most blues and greens. But if we look at a turquoise, it is very hard to say whether we should assign it to the former or the latter colour; while the sea is just as often the one as the other. The original assumption of some natural object on the borderland between the two as the concrete name-standard would quite sufficiently account for the common confusion between them in language. As a matter of fact, Mr. Whitmee informs me that the word for blue in Samoan is literally *sea-colour*. The Welsh use *glas* indiscriminately for both; and the Assyrians, according to Mr. Sayce, described green as either blue or yellow; but we know in each case that the colours themselves were or are accurately distinguished. The Quiché Indians had also one word *rax*, for green and blue; yet there can be little doubt of their proper perceptions. I believe that the same explanation must be offered of the alleged fact that the Burmese confuse these two central colours; but I have not been able myself to examine Bastian's account, and the gentlemen in Burma to whom I addressed inquiries on the subject did not reply to my circulars. At any rate, in Burmese works of art, blue and green are accurately discriminated, and blended with great taste. Certainly, Professor Blackie showed, at a meeting of the Royal Society of Edinburgh, that the Highland Scots, who call sky and grass both *gorm*, could discriminate perfectly between the two colours when tried by practical tests. It may be added that certain hues which we ordinarily class roughly together as reds, for instance that of bricks and that of some light pink geraniums, are quite as far apart from one another in consciousness as the green of the emerald and the blue of the sapphire."

Wundt[1] agrees absolutely with Grant Allen for he says that "the false conclusion from the relation between the vocabulary and the sensation has even caused people to assume that the perception of blue developed later than that of other colors because, for instance, the term for blue in Homer coincides with the one for black.[2] The error in this assumption has been demonstrated over and over again by tests on the colour sensitiveness of primitive peoples whose colour vocabulary was more rudimentary than that of the Greeks at the time of Homer."

It is quite possible that blue may have been considered unconsciously as an intermediate stage between gray and black. The blue sky certainly merges imperceptibly into gray on the one hand and into black on the other. It is something of a question what color one would call the sky on a moonlight night. Most people would say blue; but nobody could say at what point the

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[1] "Grundriss der Psychologie," 77 (1920).

[2] Lazarus Geiger: "Zur Entwicklungs-geschichte der Menschheit" (1871).

color changed to black with a waning moon or with increasing thickness of clouds over the moon. A very deep blue surface cannot be distinguished from black except in a good light.

The confusion of blue and gray is quite extraordinary so far as the everyday language of sportmen and breeders is concerned. We have blue pigeons, blue rabbits, blue Andalusian fowls, blue geese, and blue foxes, all of which are gray and not blue. There are long-haired and short-haired blue cats; and one breed of terriers, now extinct was known as blue Paul. The blue boar is really blue only on sign-posts of country inns and the blue roan horse is not blue. I have never known of blue turkeys; but I have seen what were called lavender turkeys and they were gray.

South Africa used to rejoice in the blue antelope or blauwbok, the blue-duiker, and the brindled gnu or blue wildebeest, none of which were blue. In India the case of the nilgai is especially interesting to chemists because the first syllable occurs in aniline,[1] which was so named because it was first prepared by the distillation of indigo. It is evident that all over the world it is, and has always been, the custom to confuse blue and gray, so far as the language is concerned; but I doubt very much, whether the most enthusiastic follower of Gladstone would claim that these people could not distinguish blue from gray. Blue means blue; but it is also a euphemism for gray.

In view of the fact that the flounder can duplicate red, yellow, green, and blue fairly well, it seems probable that even primitive man could also differentiate these colors though he may not have had names for them. Of course some men are color-blind; but, so far as our experience goes, there is less color-blindness among savages than among the more civilized peoples. Parenthetically it might be pointed out that it would be a very interesting and relatively easy problem for a psychologist to determine whether color-blindness occurs among flounders and, if so, whether the types are the same as among men.

Mr. Agassiz has put the matter pretty clearly. "It certainly seems to me from a physiological point of view, very hazardous to infer, as has been frequently done on philological grounds, the gradual development of the sense of color in early races of mankind, from the color descriptions of Homer and and early Greek writers. Certainly the facility for painting and coloring, noticeable in the pottery of the uncivilized races of the world seems unfavorable to this theory."

Cornell University.

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[1] Matthews: "Application of Dyestuffs", 410 (1920).

[2] Mast: Bull. Bur. Fisheries, 34, 173 (1914); Kuntz: 35, 1 (1915).

[3] G. R. Agassiz: "Letters and Recollections of Alexander Agassiz," 157 (1913).

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1-1925

NOTE ON NEGATIVE CATALYSIS

BY J. A. CHRISTIANSEN

H. S. Taylor[1] has recently proposed an interesting explanation of the phenomenon of negative catalysis in homogeneous systems based upon the supposition that the formation of molecular compounds with the negative catalyst prevents the molecules from reacting. Although this explanation is possible in some cases, it seems to me that it certainly cannot be so in others. As I discussed this problem some two years ago in a Danish paper[2] which has only been translated in part into German, I should be glad to take this opportunity of discussing the matter once more.

In recent years our knowledge of bimolecular reactions has developed so far that we are able to form a somewhat definite picture of the mechanism thereof. This knowledge can be traced back to a paper by Arrhenius[3]. The more recent development is due to Krüger[4], Goldschmidt[5], Marcelin[6], W. C. McC. Lewis[7] and others. The first condition for a reaction to occur is a collision between the two molecules in question. However, when the reaction is not immeasurably fast, only a minute friction of the colliding pairs of molecules react, viz. those whose energy exceeds a certain value. On this assumption we are able approximately to estimate the reaction and calculation shows that approximately

$$v = se^{\frac{-Q}{RT}} \qquad (1)$$

Here *s* denotes the gas-kinetic collision number and Q the mean difference between the energy of the reacting and the non-reacting pairs of molecules. The equation simply expresses that the number of molecules reacting is equal to the product of the number of colliding molecules and the probability for a pair of molecules to have the required energy.

Equation (1) has been verified experimentally in several cases and there seems at present to be no other serious objection against the underlying hypothesis than that it seems to exclude the possibility of negative catalysis. If, namely, we admit to the reacting mixture a small quantity of a foreign gas, this gas cannot alter either the number of collisions or the energy distribution of the colliding molecules appreciably, *i.e.* neither of the two factors in Equation (1). Of course the possibility exists that a certain fraction of one or both

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[1] J. Phys. Chem. 27, 322 (1923).

[2] Reaktionskinetiske Studier, Diss. Copenhagen, (1921).

[3] Z. phys. Chem. 4, 226 (1889).

[4] Göttinger Nachrichten 1908, pp. 1-19.

[5] Physik. Z. 10, 206 (1909).

[6] Ann. phys. 3, 120 (1915).

[7] J. Chem. Soc. 1915 and following years.

of the original gases can form non-reactive compounds with the foreign gas, but this fraction must be small if the ratio between the number of molecules of the latter and the former gas, respectively, is small.

This remark is important because it seems that Taylor does not grant its correctness. He compares the case with that of a warden caring for one hundred lunatics. "The wardens would be powerless were all the lunatics simultaneously violent. Only at intervals does an occasional lunatic become a candidate for a padded cell. The warden cares for him, the gentler ninety-nine do not require attention." But this analogy is false because we cannot assume the molecules of the inhibiting gas to be intelligent and combine just with those molecules which they perceive being about to react.

The possibility remains that the molecules of the inhibitor are able to prevent the elementary reaction by ternary encounters with the reacting pairs of molecules, e.g. by going off with part of the energy necessary for reaction. But just as was the case in the compound-formation theory, if the number of inhibiting molecules is small as compared with the number of the reacting ones, this effect cannot alter the reaction velocity appreciably.

Thus it seems, that homogeneous negative catalysis should be impossible if the mechanism pictured above is correct. However, it is not so because we have not yet taken into consideration the full consequences of our hypothesis. It is necessary also to take into account that the molecules of the reaction products just after the reaction possess an available energy greatly in excess of the mean energy at the temperature considered. Not only do they contain the energy (usually denoted as the critical energy) which was necessary for the reaction to occur, but, as is well known, the reaction is very often accompanied by an evolution of heat which must appear in the resulting molecules from the reaction as kinetic energy or potential energy easily transformable into kinetic.

Now these very "hot" molecules have sufficient energy to activate molecules of the reactants at the first encounter, and when these react, the resultants in their turn again are able to act as activators and so on. Consequently, it is possible that the occurrence of one elementary reaction will give rise to a whole series of such reactions.

That something like this sometimes will occur was supposed by M. Bodenstein[1] as early as in 1913, and he used this assumption (the hypothesis of "chain-reactions") to explain the velocity of the photo-chemical formation of hydrogen chloride. Later on Bodenstein himself,[2] Nernst[3] and others discussed the kinetics of such reactions in more detain and finally the hypothesis was tested experimentally by Weigert[4], who succeeded in proving it in a rather direct way, and consequently we must admit both on theoretical and experi-

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[1] Z. physik. Chem. 85, 346 (1913).

[2] Z. Elektrochem. 22, 63 (1916).

[3] Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes, p. 134 (1918).

[4] Weigert and Kellermann: Z. Elektrochem. 28, 456 (1922).

mental reasons that such chain-reactions are in fact possible. We must add that there is no reason to be seen why they should not occur also when the reaction is a thermal dark reaction.[1]

We are now able to understand the phenomenon of negative catalysis. The velocity of the chain-reaction is obviously equal to the number of chains starting per second multiplied by the number of links in each chain. We should expect that the former number could be evaluated by means of Equation (1) and consequently we cannot expect this factor to depend on the presence of small quantities of foreign molecules to any considerable degree. But the latter number obviously depends on the probability of the breaking of a chain and this probability can be altered considerably by the admixture of small quantities of a foreign gas, the molecules of which are able to take up the energy from the "hot" molecules of the reaction products or to react with them in some way or another.

A somewhat detailed discussion of the kinetics of a chain-reaction, viz. the formation of hydrogen chloride is to be found in a paper by R. Göhring[2] and also in my Danish paper. In these two papers it is shown that the oxygen according to Bodenstein's experiments and the above theory acts as an inhibitor by removing the active hydrogen molecules (or atoms?) resulting from the elementary reaction, and not by inactivating the active chlorine molecules (atoms?).

The theory enables us not only to understand the occurrence of negative catalysis but by reversing the argument we are able to discover instances of chain-reactions. If we find homogeneous reactions which are inhibited by minute quantities of foreign substances, it is often possible to conclude that chain-reactions occur in the mixture. As typical instances we might mention, besides the hydrogen chlorine reaction, the oxidation of phosphorus at ordinary temperature and the oxidations of different organic substances (e.g. acrolein) studied by Moureu and Dufraisse.[3]

Although apparently the last-mentioned reactions are not homogeneous, a more detailed analysis probably will show that they are in fact so. Also they both have the characteristics of chain-reactions to such a degree that it seems impossible to explain their peculiarities by the hypothesis that the inhibitor covers the surfaces of the oxygen acceptors.

Finally it must be remarked that the above view does not necessarily cover the case of the dissociation of oxalic acid dissolved in concentrated sulphuric acid.

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[1] In my Danish dissertation I proposed for reactions which are going on in a system in thermal equilibrium the name homothermal reactions, while reactions which are brought about by radiation (e.g. from the sun) or molecules (e.g. from a glowing wire *not* in thermal equilibrium with the reacting mixture could be named heterothermal reactions.

[2] Z. Elektrochem. **27**, 511 (1921).

[3] Compt. rend. **174**, 258 (1922); **176**, 624, 797 (1923).

As will be seen from the above the hypothesis set forth by these authors concerning the mechanism of this reaction is not sufficient to explain the inhibitory action of so small quantities of hydroquinone, but it becomes so if the occurrence of chain-reactions also is taken into account.

Contrary to what was the case in the above reactions we have here in the system a component (H_2SO_4)which is reversibly dissociable with formation of two or several substances in small concentrations, one of these being the inhibitor, in this case, water. Consequently if we assume the velocity of the reaction

$$(COOH)_2 \longrightarrow CO_2+CO+H_2O$$

to be determined by the concentration of SO_3, i.e. if the primary reaction takes place between $(COOH)_2$ and SO_3 we understand at once that a small increase in the concentration of water can give rise to decrease of the velocity on account of the displacement of the equilibrium

$$H_2SO_4 \rightleftarrows H_2O+SO_3$$

That this assumption has some reality in it we see from the remark in Bredig's[1] paper that addition of 1% SO_3 to the 100% H_2SO_4 increases the velocity to such a degree that it becomes unmeasurably fast.

On the other hand it seems to me that the mechanism of the inhibition pictured by Taylor, viz. that the water forms a comound with the sulphuric acid or (and) with the oxalic acid cannot possibly be the true one. However complete the compound-formation between the acid and the water be, water in small amounts can never appreciably alter the concentration of the substance ($(COOH)_2$ and H_2SO_4) which according to his picture determines the velocity.

Generally speaking it seems that the reaction-mechanisms in the known cases of negative catalysis are so different that they can hardly be considered from one single viewpoint but they must be divided into several classes, one of which includes the important cases of chain-reactions mentioned above.

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[1] Bredig and Lichty: Z. Elektrochem. 12, 450 (1906).

ELECTRODEPOSITION OF ANTIMONY

BY *JNANENDRA CHANDRA GHOSH AND A. N. KAPPANA*

Very little literature is available on the electrodeposition of antimony. Only two baths for this purpose appear to be quite well known for a very long time, viz: (1) the 'tartrate bath' or a hydrochloric acid solution of tartar emetic, and (2) the 'sulphide bath' which is a solution of thioantimonate of sodium or potassium. Very recently Mathers and Means[1] have published two papers on the subject. One of these deals with the examination of certain solutions containing antimony salts and the other with a new bath. This latter is a solution of antimony fluoride in water mixed with an excess of hydrofluoric acid; the authors recommend this bath as being the best one. The present investigation was undertaken with a view to make a scientific examination of the solutions already known for the deposition of antimony, to determine the exact conditions governing the formation of a satisfactory electro-deposition of the metal, and to devise a bath on a theoretical basis.

Experimental Details

The electrolytic vessel consisted of a beaker of 300 cc. capacity fixed in the middle of a constant temperature water bath. By the regulation of the size of the gas flame heating the temperature could be kept constant to within 0°.5-1°. Constant and vigorous stirring of the electrolyte was maintained throughout in all the experiments, by means of a stirrer (glass) which rested on the bottom of the beaker over a ground glass plate, and was connected to an electric motor by a thread, the rate of rotation of which was regulated by means of a high resistance rheostat put in series with the motor and connected to the mains.

The discharge potential was measured in all cases against a decinormal calomel half-element, while the electrolytic current was passing through the main circuit, no commutator arrangement being made. For this purpose the cathode used was a small strip of polished platinum 2cm × 1cm and only one antimony anode was used.

While measuring current efficiencies a silver voltameter was interposed in the circuit and was taken as standard.

Copper plates of size 5cm × 3cm were used as cathodes to test the nature of the deposits. These were highly polished and thoroughly cleansed before being introduced into the bath. While taking the deposits two antimony

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[1] Trans. Am. Electrochem. Soc. 31, 289 (1917).

anodes were used, one on each side of the cathode. These anodes were sticks about 1.5cm in width of chemically pure antimony supplied by Kahlbaum. In all cases of antimony deposition it is a very necessary condition that the anodes must be of the purest possible metal; for it was found in the course of this investigation that the anodes which were once used in the sulphide bath, when used again even after repeated cleaning, in the bath recommended at the end of this paper, hindered considerably the formation of satisfactory deposits, while fresh anodes gave an entirely good deposit. This is in all probability due to some slight traces of sulphur carried from the sulphide bath which could not be removed by cleaning the surfaces of the anodes.

The chemicals used in the experiments described in this paper were all chemically pure and were those supplied by Merck and Kahlbaum. In what follows, the term 'critical current-density' is used to mean the current density beyond which the deposit turns black.

The Examination of Some Baths

The Tartrate Bath:—Barclay and Hainsworth, in their treatise on 'Electro-plating' recommend the following bath as being a very reliable one.

Tartar emetic	4 lbs.
Hydrochloric acid	2 lbs.
Water	1 lb.

A solution of the same composition is also recommended by Gore[1]. Since tartar emetic is the starting point for this solution, it was thought necesary to examine a solution of this salt alone in water to find the difference in the nature of the deposit, caused by the addition of such a large amount of hydrochloric acid. A half-normal solution was used and deposits taken at different temperatures. The results are summarised in Table II.

TABLE I

Temp	Quality of deposit	Crit. C. D.	Current efficiency
22°.5	Very black and spongy	....	87.01%
40°	Greyish white	15 Milli-Amps	
50°	Whiter than at 40	....	87.45%
70°	Resembles dull aluminium surface	....	87.26%
90°	Perfectly white	35 Milli-Amps	93.01%

Fig. I gives the curves obtained by plotting the values for discharge potentials against current.

The solution prepared in accordance with the formula given by Barclay and Hainsworth (loc. cit.) was found to be unstable as it threw down a heavy

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[1] McMillan: "Electro-metallurgy" p. 251.

precipitate after standing for some time. A few trials showed that a solution having the following composition was quite stable and gave a brilliant white deposit.

Hydrochloric acid (S. G. 1,16. Merck)	200 cc.
Tartar emetic	100 gms
Water	100 cc.

The discharge potential and current efficiency were next determined at various temperatures up to 90°. Fig. 2 gives the discharge potential curves. The current-efficiencies are given in Table I.

TABLE II

Temperature	20°.5	40°	50°
Current Efficiency	99.9%	65.04%	31.19%

The current efficiency fell very rapidly with increase in temperature. When attempts were made to obtain a thick deposit on a copper plate, it was found that although the deposit came out uniformly for some time, big crystals began to form on the surface and prevented uniform deposition. This could not be remedied by varying current density. The deposit became worse with increase of temperature and turned somewhat black.

The Sulphide Bath:—Barclay and Hainsworth[1] give the following formula for the preparation of a sulphide bath.

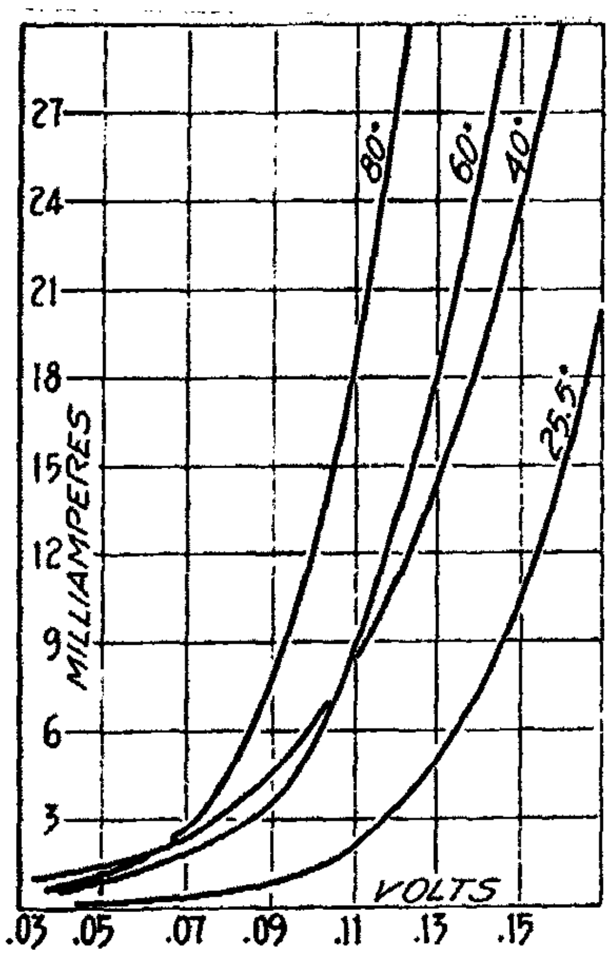

Fig. 1

Antimony trisulphide	250 gms
Sodium carbonate	500 gms
Water	5 litres.

The sodium carbonate was first dissolved in water and boiled. Antimony sulphide was next added in small quantities to the boiling solution and the whole boiled for about half an hour. The solution had to be worked while

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[1] "Electro-plating" p. 335.

boiling; but the deposit obtained on a copper plate was dark grey and did not take a good polish. The current efficiency and discharge potential were not therefore determined for this solution.

A solution of thioantimonate, prepared by dissolving a mixture of antimony trisulphide and sulphur in a saturated solution of sodium sulphide, when electrolysed at 70° and above, with the addition of some potassium cyanide, also did not give satisfactory deposit. Only thin deposits of a dark grey colour could be obtained. This solution was then diluted twice, thrice and four times and deposits taken. In no case was a satisfactory deposit obtained. Hence the current efficiency and discharge potential measurements were not made for this solution either.

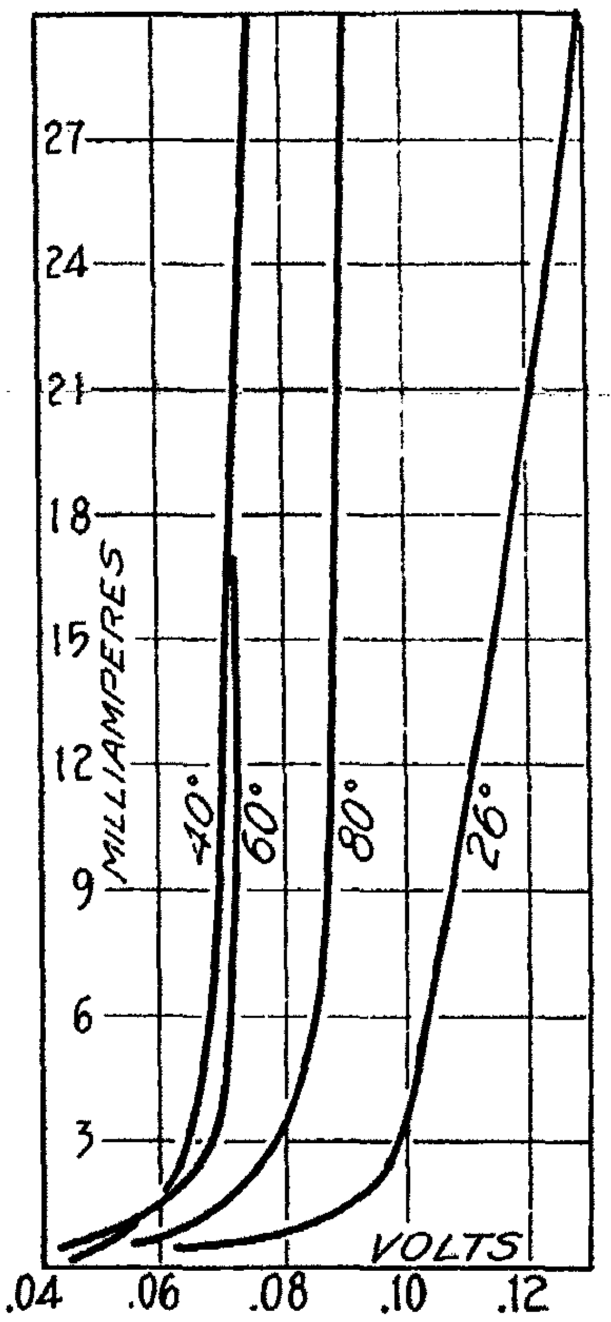

Fig. 2

The Sulphate Solution:—In the presence of a large amount of sulphuric acid, a small quantity of antimony sulphate goes into solution. This solution when electrolysed while boiling gave a fairly good deposit which took a good polish; but hydrogen was evolved very copiously at the cathode even at very low current densities and only a very thin deposit was obtained after passing the current for a long time. This solution is evidently unsuitable for purposes of electro-plating, for the current efficiency is very low.

Solutions of Antimony Trichloride in Organic Solvents:—Antimony trichloride dissolves in various organic solvents forming complex ions in solution. It was thought worth while to see if the deposit obtained from any of these solutions would be of a saitsfactory nature. Solutions were made with the following solvents:—acetone, glacial acetic acid, nitrobenzene and benzaldehyde. The best deposit was obtained from the acetic acid solution; the colour of this deposit was bluish white. Next was the one from acetone Both these deposits peeled off after three days. The other solutions gave very bad deposits. In general these solutions are unsatisfactory for use both because of their high resistance and because of the unsatisfactory nature of the deposits got from them.

The Fluoride Bath:—Finally the fluoride bath of Mathers (loc. cit.) was examined. The solution prepared for this purpose was not exactly of the same composition as the one given by Mathers and Means. Solutions of hydrofluoric acid of different concentrations ranging from one percent to twenty percent were prepared and saturated with freshly precipitated antimony oxide. The solutions were electrolysed in a glass beaker coated with paraffin; the glass stirrer was also paraffined. Deposits were first taken without the addition of any extra free HF. and then with the addition of the acid in different proportions. It was found that the fineness of the deposit was not necessarily dependent upon the concentration of antimony in the solution. In fact some of the deposits from the more dilute solutions were far finer in structure than some from more concentrated solutions. Deposits taken without the addition of free acids were in general rough and hard and took a polish with great difficulty; on the addition of free acid however the deposits became far finer. The best deposit was obtained from a solution which was first made by dissolving antimony oxide in a solution of 17% HF and to which 6% of extra acid was subsequently added. Further addition of acid to this solution did not improve the deposit, although the addition of excess of acid rendered the deposits much finer. They were quite as hard as before, for the same difficulty in polishing was experienced. The addition of small quantities of aqueous solutions of citronella and bergamot oils rendered the deposits far finer and smoother. Fig. 3 gives the discharge-potential curve for the solution of composition (17% HF solution neutralised with antimony oxide, 6% free HF). The current efficiency was found to be 99.0%.

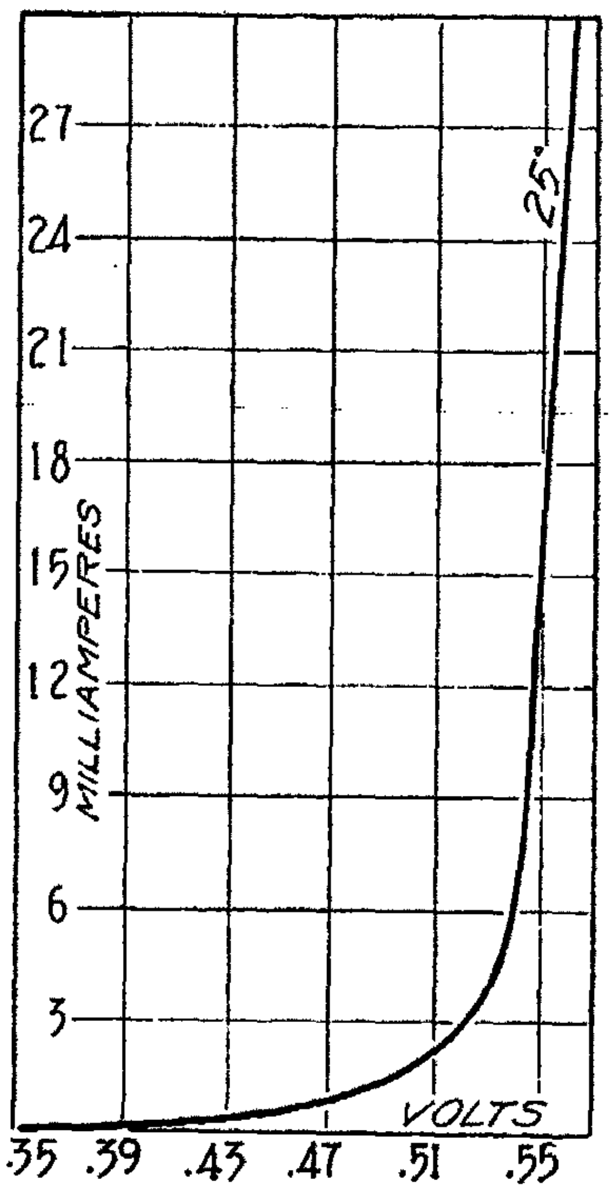

Fig. 3

Inferences from the above Examination

The deposit from tartar emetic solution alone at room temperature was found to be quite black, while the solution containing both tartar emetic and HCl gave a brilliant white deposit which was even far superior to the deposit from tartar emetic solution at 90°. This difference was evidently due to the influence of HCl.

To see if this property of improving the nature of the deposit was a peculiar characteristic of HCl, or whether acids in general could exercise this influence, the effect of the addition of a number of acids on the nature of the deposit was tested, the results of which are summarised in Table III.

TABLE III

Acid T	Temp	Quality of deposit
1. N. Tartaric acid	22°	Dark grey and smooth.
-do-	60°	Dull white and smooth.
-do-	90°	Perfectly white
2. 2.N. -do-	22°	Dull white and smooth.
-do-	60°	Slightly better than at 22°.
3. N. formic acid	22°	Whiter than the deposit taken from N. tartaric acid at 60°.
-do-	60°	Perfectly white.
4. 2N. Formic acid	22°	Quite white and smooth.
-do-	70°	Better than at 22°.
5. Monochlor-acetic	22°	Better than the deposit with N. Formic acid and brighter.
-do-	70°	Bluish white and lustrous.

The acid solutions were first prepared and then saturated with tartar emetic. These experiments proved beyond doubt, that the acids in general exercised a beneficial influence on the nature of the deposit while added to the tartar emetic bath. It was further observed that the deposit became better as the strength of the acid and the quantity added increased.

To see if the potassium ion in tartar emetic was in any way responsible for the dark colour of the deposit obtained from this solution without the addition of any acid, a deposit was taken from a solution of antimony tartrate which was prepared by dissolving antimony oxide in a boiling solution of tartaric acid. This deposit was greyish white resembling the one taken from a solution of tartar emetic in normal tartaric acid. This meant that the elimination of potassium radicle was as efficacious as the addition of extra tartaric acid to tartar emetic in improving the colour of the deposit. On the addition of hydrochloric acid to this solution of antimony tartrate the deposit became brighter and whiter; the addition of thirty percent by volume of the acid gave a brilliant mirror of antimony on a polished copper cathode. This solution appeared therefore to be superior to the tartar emetic solution containing hydrochloric acid, in so far as it required a very much lesser quantity of acid to give a deposit of even better quality.

The solution was made as follows: 500 grams of tartaric acid were dissolved in a litre of water and boiled. To the boiling solution antimony oxide was added in small quantities until no more could go into solution. To the filtered solution 30% of hydrochloric acid was added. (HCl.1.16 S.G) Solutions of lesser concentrations did not give good-looking deposits. The cathode potential and current-efficiency were next determined. Fig. 4 gives the current potential curves at various temperatures. The current efficiency varied between 95.4% and 97.1% when the temperature varied between 25° and 65°. The potential measurements showed that very low voltages were sufficient for the deposition of the metal from this solution. The critical current density was found to be 75 milli-amperes per cm^2; but current densities above 50 milli-amperes per cm were found to produce very rough surfaces.

When attempts were made to obtain thick deposits from this bath, it was found that big crystals began to form in an irregular manner on the surface. Besides it was found that the deposits on keeping for a day or two began to peel off spontaneously. Attempts were next made to remedy this defect.

Addition agents such as glue, gum arabic, gelatine, essential oils and some other organic as well as inorganic compounds have been well known to produce beneficial results in electro-plating baths. These addition agents not only improve the nature of the deposit, but also render certain non-adhesive deposits adhesive. This has been to be the case in the case of tin deposits obtained from an alkaline bath, by Mathers and Bell.[1] It was therefore hoped that by the choice of a suitable addition agent, it would be possible to obtain thick, uniformly smooth and adhesive deposit. The following substances were examined.

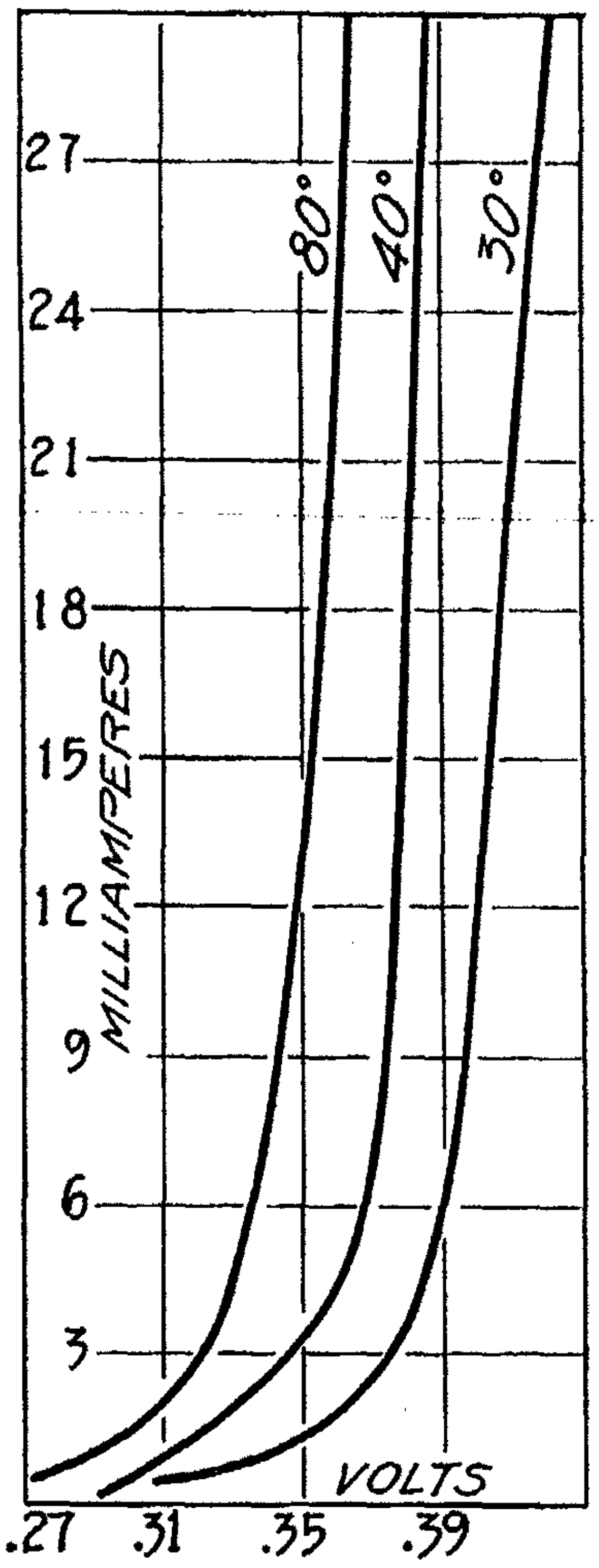

Fig. 4

(1). Gelatine, (2) glue, (3) gum arabic, (4) glucose, (5) hydrosilicofluoric acid, (6) hydrofluoric acid, (7) salicylic acid, (8) borosilicic acid, (9) resorcinol, (10) pyrogallol, (11) sodium laurate, (12) sodium oleate, (13) sodium stearate, (14) safrol, (15) eugenol, (16) geraniol, (17) cinnamic aldehyde, (18) citronella oil, (19) anise oil, (20) anethol, (21) bergamot oil, (22) castor oil, (23) oil of turpentine.

One per cent aqueous solutions of substances (1) to (4) and (7) (9) and (10) to (13) were made and added to the bath in small measured quantities. The three acids (5), (6), and (8) were added directly to the bath in small quantities. Substances (14) to (23) were all shaken very well for nearly six

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[1] Trans. Am. Electrochem. Soc. 38, 135 (1920).

hours with water and allowed to stand in separating funnels for more than a day and then the aqueous layers were separated. Small quantities of these aqueous portions were added to the bath. The following were the results:—

(10) Gelatine gave a good and adhesive deposit only once; but when the experiments were repeated a number of times the same result could not be reproduced. The deposits were in general bad and not uniform.

(2) Glue when added to the bath even in very small quantities produced fern-like figures. Addition of larger quantities did not improve the deposit in any way.

(3) Gum arabic. This gave a fairly good deposit when 8 c.c. of its solution was added to 250 c.c. of the bath. This deposit peeled off on gently striking the plate on the ground. Further additions of the solution to the bath rendered the deposits worse.

(4) Glucose. Very thin but fairly uniform deposits were obtained with this addition agent which peeled off after four days.

(5) Hydro-fluosilicic acid and (6) hydrofluoric acid did not improve the deposit. This was also the case with (7) salicylic acid.

(8) Borosilicic acid. The deposit in this case is very good but not adhesive.

(9) and (10) Resorcinol and pyrogallol gave fairly smooth deposits. These are again nonadhesive and do not take a good polish.

(11) Sodium laurate (12) oleate and (13) stearate give excellent deposits which accept a vey good polish; but these deposits fall off after a very short time.

(14) Safrol (15) eugenol and (16) geraniol made the deposit rough and crystalline.

(17) Cinnamic aldehyde gave deposits which were fairly smooth but these were not adhesive.

(18) Citronella oil. When only 2. c.c. of this solution was added to 150 c.c. of the bath, a smooth and uniform deposit was obtained which took an excellent polish; but this deposit peeled off in a day.

(19) Anise oil and (20) anethol. With these addition agents the deposits were very smooth and uniform but not adhesive.

(21) Bergamot oil. The deposit with this addition agent was the best one obtained so far and was found to be quite adhesive. However after about two months those deposits which were thick peeled off spontaneously; but the deposits, which were not very thick, adhered firmly and did not come off even on striking the deposited plates hard on the ground. The deposit improved slightly when deposited at 50°.

(22) Castor oil gave a deposit which was very bright the first few seconds it was deposited but which rolled up like paper even while the deposition was in progress.

(23) Turpentine oil did not improve the deposit in any way.

Of all the addition agents that were tested, as has been stated above, only bergamot oil gave satisfactory results. Even this addition agent could not make thick deposits stick fast. It was therefore thought necessary to see if by any other suitable manipulation it would be possible to make the deposit more adhesive.

It was believed that adhesiveness could be improved if the bright copper surface be given a thin coating of some metals which help in the formation of a solid solution at the interface which is responsible for the adhesiveness. To see if such a preliminary coating would improve the adhesiveness in any way, thin coatings of mercury, tin and cadmium were given on to the polished copper surface and antimony deposited on these. In the case of tin and cadmium, even before the current was put on, a black spongy layer of antimony began to form; however by switching on the current immediately after introducing the plates into the bath thick deposits could be obtained which were quite smooth and uniform. But these peeled off spontaneously. With mercury the deposits were quite good but peeled off after about a month.

Deposits taken on rough, instead of smooth polished surfaces were found to be adhesive even after the three months; but these also came off after striking gently. In this case also thin deposits adhered firmly.

Bismuth has almost the same discharge potential as antimony. It is therefore possible to deposit both these simultaneously from a solution containing the salts of these metals. To see if small quantities of bismuth when deposited along with antimony would make the deposit adhesive, small quantities of bismuth chloride (varying in concentration from 0.5%-0.5%) were added to the bath and deposits taken. These deposits were somewhat dark and peeled off after about a fortnight. On analysing qualitatively no traces of bismuth could be detected in the deposit.

Deposits taken from the antimony fluoride bath containing hydrofluoric acid were found to be very adhesive. It was therefore thought that adhesiveness could be imparted to the deposit from the tartrate bath while at the same time retaining the softness of the deposit, by using hydrofluoric acid in place of hydrochloric acid. Deposits were taken with various concentrations of hydrofluoric acid (1%-25%); the best deposit was obtained with 17 per cent of acid. These deposits appeared to be quite adhesive at the beginning; but, contrary to expectations they peeled off after a fortnight.

Interpretation of Results

An electrodeposit of antimony might be obtained (1) in an inhomogeneous form (powder or sponge) (2) in a coarsely crystalline form, (3) as a tough microcrystalline deposit and (4) as a bright mirror.

Beilby[1] has shown that the fine crystals on the surface layer of any specimen of antimony, under the action of the polishing lathe, pass through a liquid condition which sets to a hard enamel-like protecting coating when the polish-

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[1] "Aggregation and Flow of Solids," p. 87 (1921).

ing is finished. A bright mirror of antimony is then a congealed liquid surface. This mirror is obtained from the acid tartrate bath, only at the initial stages of electrodeposition, for small or moderate current densities. On continuing the electrolysis, the superimposed layers become minutely crystalline and fine-grained. The ions in solution resemble the gaseous state; at the beginning of electrodeposition they form a liquid layer at the cathode, which at once sets to a vitreous solid. With time crystalline forces operate to produce devitrification; microcrystalline bodies are formed in the initial vitreous layer, and the forces of orientation, thus brought into play, produce a finely crystalline structure in the superimposed layers. In this connection it is interesting to recall the experiments of Beilby which demonstrated the parallel growth of sodium nitrate crystals on a polished calcite surface. Though polishing has developed over the crystal surface a true vitreous skin, still the orienting influence of the isomorphous calcite crystals beneath could make itself felt.

Varieties (3) and (4) only are suitable from a plater's point of view, and the beneficial influence of addition agents is obvious. They are as a rule protective colloids and we have the familiar explanation that ions are deposited in a colloidal state in presence of these bodies. Mathers and Leible[1] have attempted to find a relation between the adsorption of these colloids by the plating metal and their efficiency as addition agents. It was found in most cases, that larger adsorption and greater efficiency go hand in hand. If the surface tension of liquid antimony initially deposited be diminished by the adsorption of these addition agents, the formation of small globules will be hindered. These latter possibly devitrify into crystalline specks and destroy the smoothness of the deposit. It is thus probable that addition agents produce a smooth uniform matrix of the plating metal by producing a lowering of surface tension.

Large current densities produce inhomogeneous deposits—black and spongy. Bancroft[2] suggests that large currents produce strong polarisation, the cathode film becomes dilute, resulting in the precipitation of an oxide or basic salt. Smee reached a generalisation long ago which has been supported by McMillan[3] that a deposit by a current strong enough to produce hydrogen simultaneously is dark in colour and powdery. In the case of antimony deposits, it appears however, that for moderate current densities, a black sponge is obtained at the cathode whenever it is produced there as a result of secondary chemical action and not by the primary discharge of the antimony ion, A consideration of the current potential curves will make this point clear. Pure antimony dipped in a hydrochloric acid solution of tartar emetic has been found to have an electrode potential of 0.26 volt against a decinormal calomel electrode. In Figs. 2 and 3 it will be noticed that the discharge potential plotted against electrolysing current, at first increases very rapidly and then remains constant—a curve which is characteristic of the discharge of metal ions. The discharge potential has a value varying from 0.34 to 0.37 which is

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[1] Trans. Am. Electrochem. Soc. 31, 27 (1917).
[2] J. Phys. Chem. 9, 28 (1905).
[3] "A Treatise on Electro-metallurgy," p. 205.

greater than the electrode potential of antimony in the same bath by about 0.1 volt. This difference is obviously due to what is called residual current polarisation. In HCl solution of tartar emetic or antimony tartrate, antimony is deposited by the direct discharge of $Sb^{\cdots}$ ion, and the deposit appears at first as a bright mirror and later as a fine-grained structure.

From a solution of tartar emetic only antimony is not deposited by the direct discharge of $Sb^{\cdots}$ ion as will be at once evident from Fig. 1. The abscissa representing discharge potential has a magnification 1/6th that of the 2nd and 1/3 that of the other curves, but still the current potential curve is not at all steep. Evidently this case represents the discharge of a gaseous ion on the cathode. In this case the current efficiency also did not exceed 87% up to 70° indicating that the reaction

$$C_4H_4O_6KSbO + 3H \rightarrow C_4H_4O_6KH + H_2O + Sb$$

is not complete, but that only 87% of H_2 liberated is used up in decomposing tartar emetic. The high discharge potential indicates that on an antimony surface, hydrogen has a considerable over-voltage. The contention of Smee and McMillan that simultaneous liberation of H_2 with the deposition of the metal produces dark and powdery deposits cannot be substantiated. As will be observed from Table II the current efficiency in a hydrochloric acid tartar emetic bath is only 30% at 50° though the deposit, is very bright and smooth; at 25° the current efficiency is 100%. As the current potential curve indicates the deposit is primarily that of metallic antimony. At higher temperatures a part of the precipitated metallic antimony dissolves immediately in hydrochloric acid, liberating hydrogen. The effect however from the plater's point of view is not disastrous.

Composition of the Bath

The only traceable regularity that has been generally observed is that metals deposited from solutions in which they are mostly present as complex anions, generally come down in a dense, smooth, finely-grained form. The complex anion serves as reserve for a low constant concentration of the metal cation, and prevents hydrolysis and the formation of a basic precipitate. This is also true of antimony baths, but subject to the condition that the concentration of $Sb^{\cdots}$ should be sufficient to produce antimony metal as the primary product of electrolysis. In a neutral tartar emetic solution Jordis and Meyer[1] have shown that the equilibrium concentration of $Sb^{\cdots}$ ion due to the reaction $C_4H_4O_6KOSb + 3H$ (present in pure water)

$$C_4H_4O_6KH + H_2O + Sb^{\cdots}$$

is very small. Hence it is intelligible that Sb is$^{\cdots}$ not discharged at the cathode. With addition of acid, $Sb^{\cdots}$ is obtained in increased concentration resulting in its primary discharge and producing an improved deposit.

Antimony fluoride has a far greater tendency towards complex formation than the other halides, complex salts like $KSbF_4$, $NaSbF_4 . 2NaF$, are common

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[1] Z. angew. Chem. 17, 169, 204, 236 (1904).

where the antimony exists as a negative ion the equilibrium concentration of $Sb^{\cdot\cdot\cdot}$ ion due to the dissociation of the complex SbF_4 is much greater than in the neutral tartar emetic solution. Antimony is obtained as a primary deposit as the steep nature of the current potential curve in Fig. 3 B indicates. The discharge potential is much higher than the electrode potential of antimony in normal antimony chloride solution. This is partly due to residual current polarisation and to the very small concentration of $Sb^{\cdot\cdot\cdot}$ present as such in the acid fluoride bath.

Influence of Temperature

In an acid tartar emetic bath the current efficiency fell from 100% to 30% as the temperature was raised from 25°-50°; while in an acid antimony tartrate bath, the current efficiency remained pretty nearly constant at 97%. No satisfactory explanation is available unless it be that potassium has a marked catalytic action on the solution of antimony by hydrochloric acid. The advantage of the latter bath is obvious, for it does not require any regulation of temperature.

Conclusion

The composition of the acid tartrate bath has been arrived at on theoretical grounds after a critical examination of the baths already known as well as certain other solutions. With oil of bergamot as addition agent this bath gives a very smooth, uniform nice white deposit, which on polishing assumes a silvery appearance. Thin deposits of thickness 0.025, mm have been found to be quite adhesive; this thickness is quite sufficient for plating purposes. High current densities can be employed (50 milli-amperes per cm) and the current efficiency is as high as 97%. These and other points of advantage mentioned in the paper above, mark the bath as specially suitable for plating on a large scale.

THE PREPARATION OF MEMBRANES WITH UNIFORM DISTRIBUTION OF PORES

F. E. BARTELL AND M. VAN LOO[1]

In a recent paper by Bartell and Carpenter[2] methods were given for the preparation of collodion membranes. It was found to be possible to prepare different membranes with practically the same degree of permeability. It was also shown that membranes of the same or of different permeability, having in every case practically the same number of pores per given area of membrane could be prepared. This was proven through the agreement between the relative pore diameters as measured and as calculated according to Jurin's law and according to Poiseuille's law. When Poiseuille's formula $Q = KnPD^4T/L$ was applied and the value n (representing number of pores per given area) kept constant, results for D, the pore diameter, were in every case in close agreement for the pore diameter as calculated by the method based upon Jurin's law. This result was a bit surprising, until a study of the behavior of the material during the course of the setting of the membrane was carried out.

In the following table results are given which show the relative pore diameters as determined by the Jurin Law method and by the Poiseuille Law method.

MEMBRANE PORE SIZE

	Relative Permeability	Pore diam. in microns (Jurin's Law)	Relative Pore Diameters	
			Jurin's Law Method	Poiseuille's Law Method
Least permeable membrane	1.	0.701	1.00	1.00
Medium permeable membrane	1.978	0.934	1.33	1.38
Very permeable membrane	7.353	1.681	2.39	2.31

During the course of the original work, and subsequently in later study, it was observed that our most satisfactory methods gave us membranes with a surface exhibiting distinctly cellular configurations. The surface appeared to be covered with a fine net-work of honey-comb structure of remarkable uniformity, if proper care were taken to avoid disturbing air currents, etc. Subsequent observation of the drying and setting of similar systems, composed of volatile and non-volatile components, in which we employed readily visible solid particles in suspension, enabled us to arrive at an explanation of the mechanics involved in the formation of such configurations as above noted.

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[1] Holder of Acme White Lead and Color Works Fellowship.

[2] J. Phys. Chem. 27, 252-269 (1923). See also ibid. 27, 101-116 (1923).

When such a system is observed microscopically during the course of the drying, it is found that the escape of the volatile gives rise to a distinct vortex action. When the film is first applied to the microscope slide, the surface appears to be in rather violent motion, of a somewhat random nature. Almost at once, however, the surface becomes raised in certain places over the entire area of the film. It then becomes evident that the volatile is escaping from the apices of these rounded surfaces, leading to a regular vortex action with these apices as centers. Due to the practical impossibility of producing a liquid medium with perfectly uniform distribution of the volatile, and of maintaining absolutely uniform conditions of evaporation, certain of these vortices are stronger than others, and overcome them. As a result of the redistribution of the forces, the film progresses from the stage of a large number of small vortices to a uniform arrangement of a small number of more powerful ones, similar in magnitude of strength. Since such vortex action sets up curved surfaces, by the mutual thrust of these surfaces, one on the other, there results a condition of closest packing, i.e. each one is in contact with six others at the surface. Hence, the surface appears as an area of hexagonal cells.

In the case of colored suspensions in a similar system made up of a non-volatile plus a high concentration of a readily volatile constituent, a comparatively clear spot appears in the center of each cell. The individual particles of the suspended matter come up through the center of each vortex, pass radially outward along the surface of the cell, then downward at the cell wall, then inward along the bottom of the cell to the center, where they may again pass upward and repeat the circuit. Similar circuits appear in the interior of the cell where particles may be entrained in surrounding circuits, and eventually appear at the surface. Each cell, of course, comprises one vortex —more exactly, a modified vortex-ring. Fig. 1 below shows a section of the surface, illustrating the formation of hexagonal cells, as a result of the impression of six adjacent vortices on one vortex, and indicates the motion of the suspended particles at the surface. Fig. 2. shows a cross-section of a cell,—the

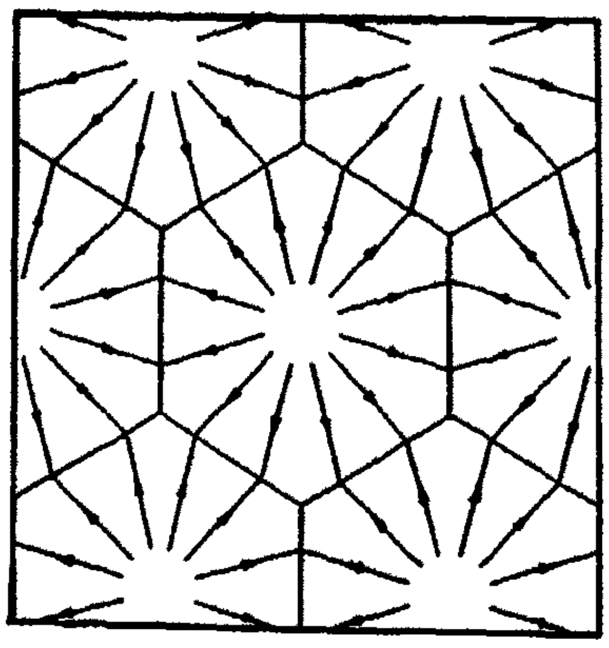

Fig. 1

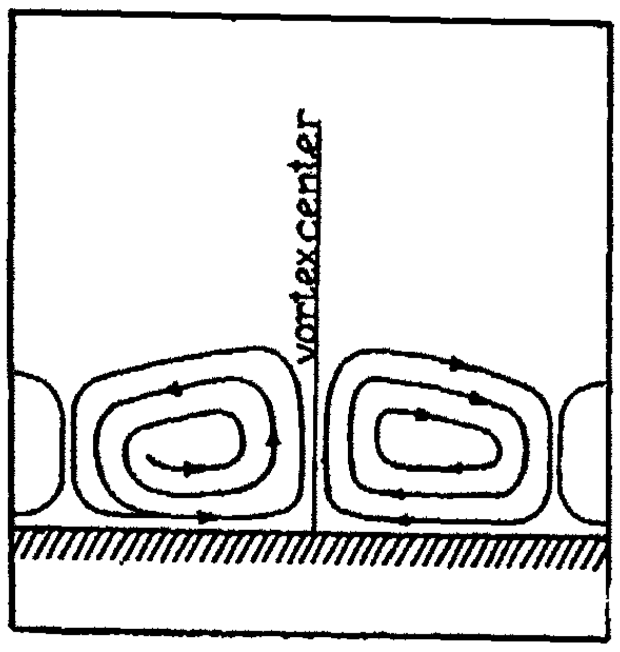

Fig. 2

right half showing complete circuits and the left, the possible entrainment of suspended particles from the center to the exterior circuits.

A similar phenomenon of vortex action has been described by other observers. Kerr Grant[1] reported vortex action in emulsions of radio-active minerals in alcohol, etc., Prof. James Thomson[2] observed the same cellular structure, due to convection currents in soapy water; E. H. Weber[3] in 1885 observed the same cellular arrangement of convection currents in emulsions, as described in O. Lehmann's "Molekular-physik". Harold Wager[4] reported the same with minute mobile organisms in water, while W. M. Flinders Petrie[5] reported this type of surface arrangement in suspensions of powered Oriental coffee in milk and water. B. A. Keen[6] observed it in suspensions of clay in ammonia and in alcohol. M. Henri Benard[7] has done considerable work on vortex motion in cells, using convection currents as the agents for producing the same effect in permanent media, such as paraffin, etc. The earliest reference we found to this phenomenon was that mentioned by Korteweg[8]—the notes of Christian Huygens reprinted in his "Oeuvres"—where he describes exactly this vortex motion in drops of urine on talc, under the date of Sept. 5, 1678.

When a collodion film is prepared, such a vortex action as above described, always occurs. The average collodion film used in osmotic work represents the stage of uniform distribution of the stronger vortices,—the stage subsequent to the transition from the large number of smaller cells to the limited number of large cells, as above described. Hence, the number of cells in the average membrane are the same when prepared in a uniform fashion as described by Bartell and Carpenter. That the center of each cell represents a pore in the membrane will be understood from the following, somewhat superficial explanation, which is based on a study of the mechanics of the removal of the volatile, during the setting of the membrane.

At the instant of the application of the film of liquid, a certain amount of evaporation of the volatile occurs from practically all points on the surface. Such an evaporation cools the surface, and increases its density relative to the body of the film, because of the decrease in the concentration of the volatile. These two effects, the temperature gradient, and the density gradient, both tend to set up vertical convection currents through the film. These currents naturally suffer deflection from the true vertical as a result of a number of causes. There are always certain solid or semi-solid particles suspended throughout the body of the medium, around which the currents must pass. Furthermore, any variation in the concentration of the volatile as a result of the impossibility of effecting a perfectly homogeneous mixture of all the con-

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[1] Nature, 93, 162 (1914)
[2] Nature, 93, 213 (1914)
[3] Nature, 93, 213 (1914)
[4] Nature, 93, 240 (1914)
[5] Nature, 93, 269 (1914)
[6] Nature, 93, 321 (1914)
[7] Nature, 93, 584 (1914)
[8] Ann. Chim. Phys., 23, 62-144 (1901)

stituents, tends to set up horizontal diffusion currents as well. Hence we have horizontal as well as vertical components of motion set up, and a vortex-ring results.

It is apparent that in the upper part of the circuit the moving liquid is exposed to the air, and must continually lose volatile, which it then partially recovers by diffusion, etc., in passing around the lower part of its path. Hence, the center of the cell represents the point of maximum volatilization, as here the concentration of the volatile is the highest, while the cell wall marks the lowest point in concentration of the volatile constituent. The prerequisite conditions for the maintenance of the vortex action are thus continuous, although decreasing in relative magnitude. Initially, of course, we have a considerable area of liquid at the center of the cell with a very high concentration of the volatile. This area decreases as the total concentration of the volatile diminishes, i.e., as the violence of the vortex action decreases. In the original work, water was added after certain intervals of time, to remove the remaining volatile, which would leave an opening or pore at the center of each cell. The size of this pore is proportional to the amount of volatile present at the time the water was added, and hence, the permeability (which is largely dependent on the pore diameter) is closely related to the time element in the experimental manipulation.

There is continually a gravitational force on the solid suspended particles which would lead them to flow into the centers of the cells as the violence of the vortex action decreases. In fact, if the system retains sufficient fluidity subsequent to the removal of most of the volatile to permit such an action, the surface tension effects and the gravitational effects may cause the central portions of the cells to close in, and in extreme cases completely eradicate the cell structure. As we have said, to prevent such an action, in the original work on collodion membranes in this laboratory, water was added to remove the volatile before the porosity had decreased too far. A membrane of sufficient rigidity to maintain a permanent configuration was thus obtained. It is at once apparent, in the light of the above discussion, that the porosity or permeability of membranes can be reproduced or varied at will by arresting the vortex action at the proper stage. That was exactly the function of the water.

From the above described experiments, it seems entirely reasonable that the number of hexagonal cells within a given area of surface determines the number of pores which open into that surface. *It must follow that, with a system of a given composition at a definite temperature, the distribution of the pores will be the same in any membrane prepared from that system under comparable conditions.* From the nature of their composition, the membranes produced as in the work cited must of necessity have the same number of pores per given area. Therefore, the original assumption to that effect is corroborated. The different degrees of permeability obtained through the removal of the volatile at different stages, is easily accounted for in our experiments, through the fact that the vortex action is arrested in varying states of activity.

Summary

1. Previous work by Bartell and Carpenter has shown that membranes with different degrees of permeability may be prepared with the same number of pores per given area of membrane.

2. Our study has shown that as a result of vortex action in drying, collodion membranes have a cellular structure. It is assumed that the pores in the membranes are the centers of the cells, so that the number of cells determines the number of pores. Membranes prepared from the same medium have the same number of cells per given area, and therefore, the same number of pores.

3. The permeability, which is largely dependent on the pore diameter, may be varied by arresting the vortex action at different states, by the removal of the volatile.

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THE ACCURATE CALIBRATION OF CAPILLARY TUBES

19- 696

BY K. J. ISAAC AND IRVINE MASSON

In connexion with work on the compressibility of gaseous mixtures by Dolley and one of us,[1] it was found that the methods of ascertaining the bore or volume of capillary glass tubes, described in the literature, are generally subject to serious errors. Improved methods were therefore worked out which enabled us to know the volume of any length of a 50cm. capillary of about 1 mm. bore with an accuracy of one part in several thousand. The most convenient of these methods is here described, because similar knowledge is required for many purposes, and it is hoped that other workers may thereby be saved considerable labour.

It may be premised that the tubes with which we are concerned are closed at one end of the capillary, a fact which calls for certain experimental arrangements whose simplification will be obvious to anyone who applies the general method to tubes which can be left open at both ends.

Mercury is used as the calibrating fluid; and we have found the very simple method described by Dixon and McKee[2] to be entirely adequate. No process of measurement which involves *horizontal* threads of mercury is reliable, since in such a thread the meniscus sags, and its volume cannot be estimated; further, the shape is variable from point to point even in clean tubes of small bore, so that its effect does not cancel out in successive measurements of length. Consequently the tube must be used and calibrated vertically; and in this case, since the diameter of the tube is approximately known, measurement of the height of the meniscus affords a very close estimate of its volume when the data of Schalkwijk[3] are applied.

The clean, dry, and dust-free tube is mounted, as shown in Fig. 1, in a jacket kept at constant temperature, preferably that at which the tube is eventually to be used. In our tubes, direct graduation was not permissible, since they would have been less able to resist high internal pressures; a light glass scale was therefore attached to each tube, during calibration and use, by means of tight rubber bands. Relative movement of scale and tube is guarded against by taking readings of the external top end of the tube, which point serves as the zero mark in all the measurements.

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[1] Masson: Proc. Roy. Soc. **103** A, 524 (1923)

[2] J. Chem. Soc. **123**, 895 (1923)

[3] Comm Phys. Lab. Leiden, No. 67 (1901); Verslag. Kon. Akad. Wet. Amst., **1900**, p. 462; **1901**, 512.

Whatever reading-instrument is used in conjunction with the scale must provide measurements of height-differences which are reliable to about 0.01 mm. We use a telescope provided with a spirit-level and with a Hilger micrometer eyepiece, which gives about 100 drum-divisions per millimetre read at a distance of several feet.

The foot of the capillary, which is to be dispensed with when the tube is eventually in actual use, passes through the bung of the jacket and carries the side tube with tap B, besides having a capillary tap C whose stem is drawn out to a very fine jet. This stem also bears a small rubber cork for the attachment of the weighing-vessel A. The tap B communicates with a high-vacuum pump, such as one of the mercury condensation type; doubtless a Toepler pump combined with a cooled charcoal bulb would also serve.

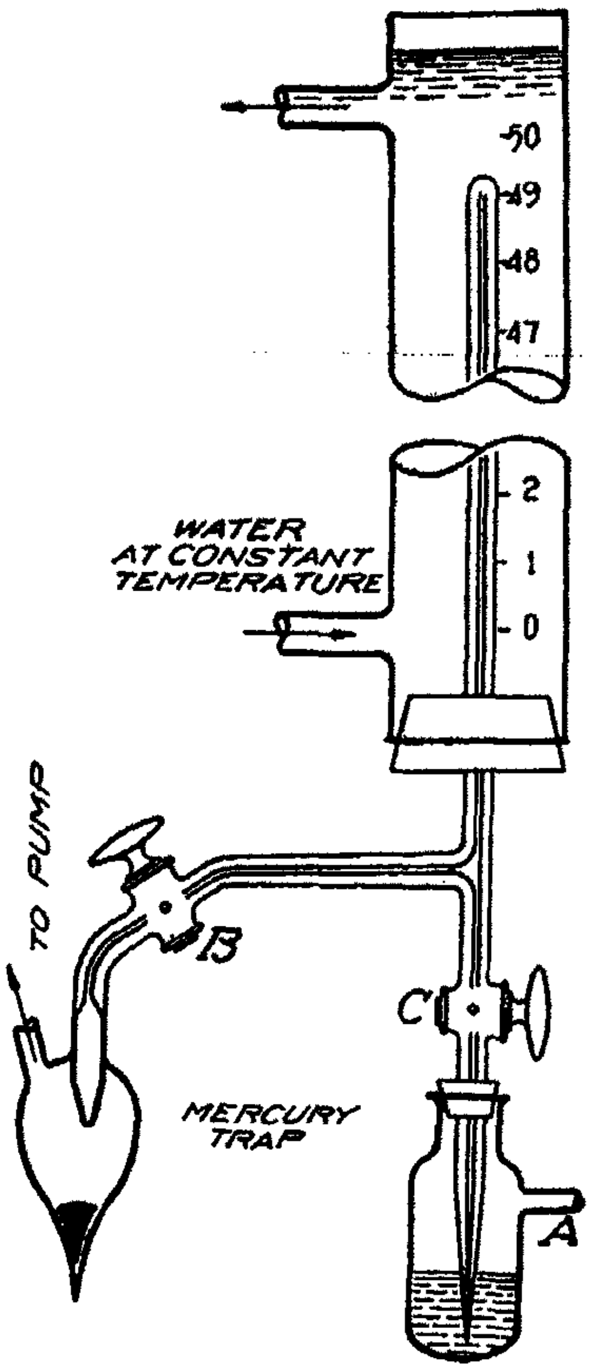

Fig. 1

The vessel A, containing pure mercury, is placed in position, and a Fleuss or other oil vacuum pump is temporarily connected with its side arm by a rubber tube. Taps B and C are opened and the tube is exhausted, the oil pump serving to prevent the mercury from rising as far as tap C. When exhaustion is complete, the taps are shut and the oil pump is disconnected; tap C is now opened slowly until the mercury has risen just above it, when the exhaustion is continued for a while in order to remove any air trapped at the opening. Tap B is then finally closed and the mercury is allowed to rise to a point convenient for the lowest reading of level.

The jacket temperature, the level of the tip of the meniscus, and the height of the meniscus, are noted. The vessel A is removed, weighed, and replaced.

The oil pump is re-connected, and a partial vacuum is produced in A so that when C is opened the mercury falls slightly; this is necessary in order to remove any trapped air from the jet. C is closed, the oil pump is removed, and the mercury is allowed to rise to a new level about 2cm. above the first; a fresh set of readings of heights and weight is then taken. This process is repeated at intervals of about 2cm. until the tube is completely full of mercury. If the tube be of height greater than the barometric, a cycle pump can replace the oil pump in the last stages.

This completes the first calibration; and the mercury is now to be drawn down again, and a second calibration is made in the same way, the intervals overlapping those of the first set.

Finally, a single "overall" determination is made as a check, one weighing being made when the tube is completely full and the other when the mercury has been withdrawn and then allowed to rise to near the lowest mark. A "rising" meniscus is better-shaped than a "falling", hence the need for the latter manoeuvre.

Calculation. All distances along the capillary are measured from the external top of the tube. The observations of temperature, heights, and weight of mercury being recorded tabularly, each set is treated thus:—From the data of Schalkwijk (loc. cit.) a table can readily be drawn up to show the volume, and hence the equivalent cylindrical height, of any mercury meniscus of measured height in a tube of approximately known bore. (For 1 mm. tubes, the equivalent cylinder has practically one half the height of the meniscus). The observed level of the mercury is, accordingly, corrected to what it would be if its surface were flat. These corrected distances, each about 2cm. apart, correspond with the measured weights of mercury, and hence with volumes, due corrections being of course applied for buoyancy, scale-errors, and the like. The mean cross section or volume per linear centimetre within each of these 2cm. sections is thus found, and the values are plotted on squared paper, using the distances from the external end of the tube as abscissae. The "curve" takes the form of a series of steps, the horizontal lines marking the mean vol./cm. between the points indicated by the vertical lines. A smooth curve is now drawn through the mid-points of the vertical lines of the steps, and this shows the vols. per cm. along the length of the tube to near the closed end.

The results of the second calibration are now drawn in the same way on the same paper. A mean curve is then drawn, by eye, between the two. The usual maximum deviation of either curve from the mean is little more than 0.00001 cm.^{2}, so that from the mean curve may be read, with great exactness, the cross section at any point. By summation, the aggregate volume of the tube is obtained, and is compared with the experimental "overall" aggregate. Any difference—and we find differences of not more than 1 in 6000—is distributed proportionally over the length of the tube, as being probably due to cumulative error in the meniscus-correction; and so the final table is drawn up. This shows, for each cm. of the tube, the total volume and the mean volume between it and the point 1 cm. beyond it, which interval in the case of ordinarily uniform tubes is ample for purposes of calibration.

It may, finally, be mentioned that we have re-calibrated some of our tubes after they had been used for some months in experiments at 25° up to 130 atmospheres pressure, without finding any significant change in capacity; nor do they suffer detectable temporary dilatation during exposure to 10 atm. internal pressure. The accuracy secured by the method of calibration is thus not illusory.

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THE EFFECT OF THE CONCENTRATION OF COLLOIDAL CLAY UPON ITS HYDROGEN ION CONCENTRATION[1]

BY RICHARD BRADFIELD

In a recent study of the effect of the soil-water ratio upon the H-ion concentration of soil mixtures, Salter and Morgan[2] found with most of the soils studied a logarithmical relationship which could be made to satisfy the adsorption isotherm of Freundlich. Since some of the solid phase remained undissolved at all dilutions, they conclude that their results "discredit any theory of soil acidity which assumes that the acid reaction is due to highly insoluble acids, either organic or inorganic which must under conditions of equilibrium form a saturated solution and give an approximately constant H-ion concentration." They believe instead that the acidity must be due to the preferential adsorption of the OH-ion by soil colloids.

Recent work in this Laboratory on the nature of the acidity of the colloidal clay extracted from an acid soil indicates that this material acts in many respects as a true acid. It has long been known that soils have many properties which are peculiar to colloidal systems. Few attempts were made until recently to separate the more active colloidal fraction from the relatively inert non-colloidal material which makes up the great bulk of the soil mass. Moore, Fry and Middleton[3] have found that the amount of colloidal material in soils is much larger than had previously been supposed. Stevenson[4], Knight[5] and others have shown that the buffer action and titratable acidity of soils is proportional to the amount of colloidal material present. Soil acidity is considered due to the leaching of bases from the complex mineral silicates. If that is true it would be quite logical to expect to find that the colloidal fraction of soils would be the most thoroly weathered and consequently the most strongly acid.

It has been found[6] that if dilute standard solutions of strong bases are titrated with acid colloidal clays by either the conductivity method or the hydrogen electrode method, that definite end points can be obtained, that equivalent quantities of bases are neutralized by equal amounts of the colloidal acid, and that the curves obtained by both methods are of the type that are characteristic of the neutralization of a strong base by a weak acid. By means of such measurements it becomes possible to assign a definite normality to the colloidal acid.

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[1] A Contribution from the Soils Laboratory, Agricultural Experiment Station. University of Missouri.

[2] J. Phys. Chem. 27, 117-40 (1923).

[3] J. Ind. Eng. Chem. 13, 527-30 (1921).

[4] Soil Science, 12, 145 (1921).

[5] J. Ind. Eng. Chem., 12, 465 (1920).

[6] Bradfield: J. Am. Chem. Soc. 45, 2669-87 (1923).

That the acid colloidal clay is a true acid has been substantiated further by studies of the relation between H-ion concentration and the flocculation of an acid colloidal clay. The electrolyte requirement[1] was found to increase about ten-fold in the case of potassium mixtures when the Sörensen value was changed from 6.5 to 8.5. Further increases in alkalinity were without effect, indicating that the acid colloidal clay had been neutralized and all converted into the K salt. After the salt had been formed, the excess of OH-ions had no influence upon the amount of K-ions required to produce flocculation. Neutral colloidal clays were found to show no such change in electrolyte requirement as the H-ion concentration was changed, due apparently to the fact that in the case of such clays there was no appreciable acidity to be neutralized by the OH-ion and consequently KOH was about as efficient as a flocculant as KCl.

A study of the effect of the H-ion concentration upon the absorption of bases by the acid colloidal clay shows that there is a very marked increase in the amount of base absorbed when the pH value is raised above the neutral point, then becomes about constant, which likewise indicates that a true neutralization of the acid colloid has taken place. Gordon and Starkey[2] found a simialr relationship between the H-ion concentration and the absorption of K by silica gel.

Salter and Morgan discredit the true acid theory of soil acidity because they found an exponential relation between the H-ion concentration and the soil-water ratio. Their conclusions were based upon the supposition that they were dealing with a saturated solution of any soil acid which might be present. This assumption is not necessarily true. The soil is a complex system made up largely of relatively coarse, inert particles which are coated over more or less, by a layer of colloidal material. If soil acidity is due largely to this colloidal fraction, it does not follow that the mixture is saturated with the soil acid. because some of the coarser, inert, crystalline material, such as quartz, remains undissolved. In fact, it would seem highly improbable that the amount of active colloidal acid should reach the saturation point even in the most concentrated mixtures studied by them. The curves indicate that such a point is being approached. It is of interest to note also that the two soils which seemed abnormal were the only clays and consequently the only highly colloidal soils studied. In the case of these soils at the higher concentration (17.880 to 1000 g of soil per liter H_2O) the depression of the H-ion concentration was so great that it was "impossible to calculate an adsorption isotherm which would satisfy any three points on the curve." This would seem to indicate that, in the case of these highly colloidal soils, the concentration of the colloidal acid was approaching rather closely the point at which the H-ion concentration would become constant.

The fact that certain data can be fitted to an adsorption isotherm does not necessarily indicate that the relationship is caused by adsorption. The

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[1] Bradfield: J. Am. Chem. Soc. 45, 1243-50 (1922).

[2] Soil Science, 14, 1-7 (1922).

Freundlich equation is purely empirical and as pointed out by Fisher,[1] by altering the constants involved, a series of curves can be obtained which will fit nearly any set of experimental points with the desired degree of accuracy. In his study of the effect of dilution upon the H-ion concentration of acetic acid Walpole[2] found that the relationship was exponential at the concentrations studied. In fact, most acids show the same tendency noted by Salter and Morgan, to increase in H-ion concentration with increased acid concentration, but at a slower rate, in concentrations above that known as infinite dilution, at which point dissociation becomes complete and the relationship linear. The curves of Salter and Morgan become practically linear at the higher dilutions.

If soil acidity is due to a true acid of colloidal dimensions, as the work cited above indicates, it would seem that the failure of Salter and Morgan to obtain a constant H-ion concentration at even the 1:1 soil-water ratio might be due to the fact that the colloid content of these soils was so low that the concentration required for the constant H-ion concentration could not be reached. If this were true it should be possible to attain the desired concentration by eliminating the relatively inert coarse material which makes up the bulk of the soil and working with the colloidal material itself. This study includes therefore, the preparation of a concentrated solution of acid colloidal clay, a study of the effect of dilution upon its H-ion concentration and a similar study of the effect of dilution upon the H-ion concentration of acetic acid to be used for comparison.

Experimental

A fresh, acid clay soil was suspended in five parts distilled water by churning for three hours in an ordinary barrel churn. No deflocculant was used because any chemical added to the soil in sufficient quantities to deflocculate it will cause considerable alteration in its natural properties. It was found[3] that, if a fresh soil were used about the same amount of colloidal material could be recovered without the use of a deflocculant as could be separated from an air-dry soil with a deflocculant. The suspension was allowed to settle undisturbed for ten days to eliminate the coarsest of the non-colloidal material. The fraction still in suspension was siphoned off and passed, at the rate of one liter per minute, thru a Sharples super-centrifuge, generating a centrifugal force of 30,000 times gravity. This application was sufficient to remove the great bulk of the non-colloidal material. The solution was then passed thru the centrifuge a second time at the rate of twenty liters per hour. The solution emerging was truly colloidal, perfectly clear when examined by transmitted light and showed no tendency whatsoever to settle out on prolonged standing. This solution contained about one percent of oven-dry (105°) material. In order to obtain the concentrated solutions desired for this study, this dilute colloid was passed thru the centrifuge at the rate of one liter

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[1] Trans. Faraday Soc. **17**, II, 310 (1922).
[2] J. Chem. Soc. **105**, II, 2521 (1914).
[3] Bradfield: Missouri Ag. Ex. Sta. Res. Bull. 60 (1923).

per hour. This prolonged application of the high centrifugal force was sufficient to deposit the great bulk of the colloidal material upon a celluloid sleeve placed inside the centrifuge bowl. After a sufficient amount had been deposited, the sleeve was removed and the colloid, now having much the consistency of ordinary axle grease, scraped off by means of a spatula.

After a sufficient amount of this material had been obtained, it was diluted with water until it had the consistency of a very thick sirup. This solution was found to contain 12.8% of oven dry material. Dilutions containing 6.4%, 3.2%, 1.6%, 0.8%, 0.4%, 0.2%, 0.1%, 0.05% and 0.025% were prepared from this stock solution and their H-ion concentrations determined by the hydrogen electrode method, using a Type "K" Leeds and Northrup potentiometer, a saturated KCl calomel electrode and a modification of the Hildebrand type of hydrogen electrode. All measurements were made at about 25° in an inside basement room of rather constant temperature. The water used for the dilutions was ordinary distilled water which when freed from CO_2 was slightly alkaline: the Sörensen value was about 7.45. A series of acetic acid mixtures was prepared using as a base a 0.1078 normal solution and diluting to half the original concentration each time. The H-ion concentration of both the acetic acid and the acid colloidal clay series were measured simultaneously against the same calomel electrode. The data are presented in Table I and graphically in Fig. 1.

TABLE I

The Effect of Concentration upon the H-ion Concentration of the Colloidal Clay Acid and Acetic Acid

Colloidal Clay Acid		Acetic Acid	
Concentration in percent of oven dry material	PH	Concentration in normality	PH
12.8	4.02	.1078	2.88
6.4	4.10	.0539	3.03
3.2	4.15	.0269	3.14
1.6	4.30	.0134	3.30
.8	4.50	.0067	3.43
.4	4.85	.0033	3.61
.2	6.26	.0016	3.85
.1	6.93	.0008	3.91
.05	7.15	.0004	4.18
.025	7.30	.0002	4.40
H_2O used	7.45	.0001	4.73
		.00005	5.40
		.000025	5.86

Discussion of Results

The portion of the colloidal clay curve for concentrations up to 2-3% (Fig. 1.) is almost identical in form with those of Salter and Morgan. With higher concentrations the curve flattens and the pH value becomes almost constant. The similarity between the acetic acid and the colloidal clay curves is so striking as to make it seem highly improbably that in the case of the former, we are dealing with a true acid and in the case of the latter, not with an acid, but an adsorption phenomenon. The concentration of colloidal material in soils is such that it is only in the exceptionally heavy clay soils that the flat region of the curve is reached even at the 1:1 soil-water ratio. Rice and Osugi[1] found that the amount of sugar inverted by an acid soil was greatly increased by increasing the ratio of soil to water. The H-ion concentration of the colloid-free aqueous extracts of these soils was found to be neutral. Salter and Morgan lay this observation to faulty technique? But it is quite well known that the colloid-free aqueous extracts of soils when carefully freed from CO_2 are frequently acid free. The results of Rice and Osugi are exactly what would be expected if they were dealing with an acidity due to colloidal acids.

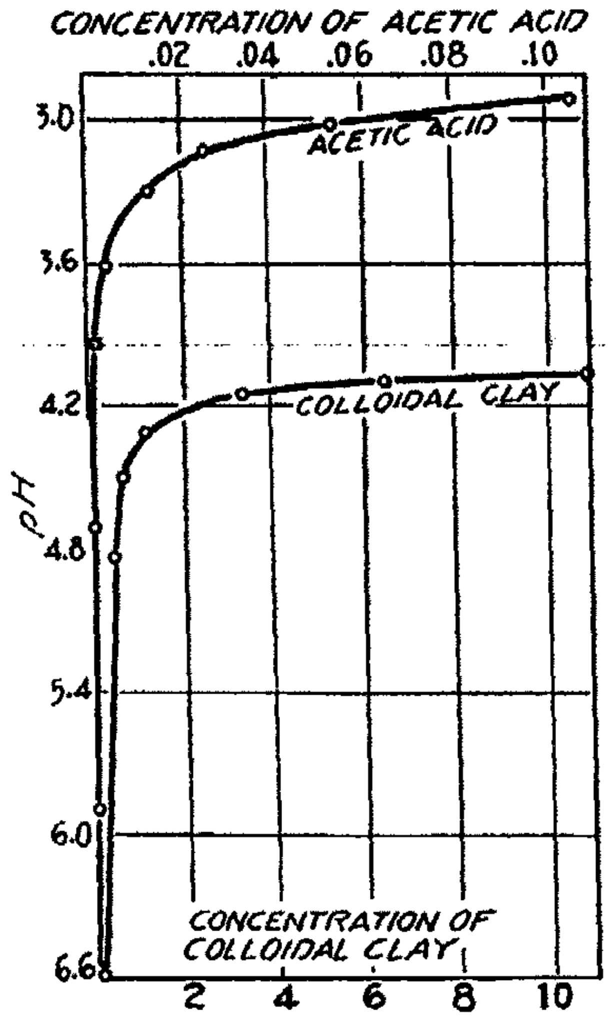

Fig. 1

The Effect of Concentrationof Colliodal Clay and Acetic Acid upon H-ion Concentration.

The mineral acid theory of soil acidity has not been as widely accepted as it seems to deserve because its advocates have always been searching for an acid, the particles of which were of ordinary crystalloidal dimensions. When we consider the great complexity of the soil minerals, which are salts of the soil acids it would seem much more likely that the acid would be so complex and the molecules so large, that they would reach colloidal size. In fact, silicic acid, the simplest possible acid of this group is stable only when in colloidal condition. It may be prepared as a crystalloid but rapidly changes to a colloid on standing.

Conclusions

The relation between the concentration of an acid colloidal clay and its H-ion concentration is practically linear at higher dilution (0—0.4%), exponential at intermediate dilutions and (0.49—3.5%) practically constant at higher concentrations (3.5—12.8%). The curve of the acid colloidal clay and

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[1] Soil Science, 5, 333-59 (1918).

that of acetic acid are so similar in every respect that it seems highly improbable that the acidity in the case of the former is due to the preferential adsorption of the OH-ion and in the case of the latter to true acidity. The differences in the Sörensen values yielded by the two acids are probably due to differences in their strength, the colloidal clay acid being a much weaker acid than acetic. The fact that one is colloidal and the other crystalloidal is due merely to differences in the complexity of their molecules and not to any fundamental difference in the nature of their acidity.

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NOTE ON COLLOIDAL NICKEL HYDROXIDE

BY O. F. TOWER

In an article[1] published about a year ago reference was made to the peculiar behavior of nickel hydroxide formed in a glycerine solution. This has been investigated further in order to ascertain what concentrations of the constituents are necessary to bring about the results observed.

In the first place a solution was prepared containing 4 grams $Ni(C_2H_3O_2)_2 . 4H_2O$ in 100 c.c. of Baker's C. P. glycerine. The most favorable conditions for reproducing the behavior just referred to were obtained by mixing 16 c.c. of this solution with 8 c.c. of normal potassium hydroxide in alcohol. This set to a jelly within 24 hours and later syneresis began, sometimes slower, sometimes faster, but in general the same stages were observed as described in the previous paper. In case relatively less of the potassium hydroxide solution were employed, either no jelly formed or only a very mobile one; with more potassium hydroxide solution, the jelly was much firmer but little or no syneresis occurred.

Two new methods of preparing colloidal nickel hydroxide will now be described.

1. To 24 c.c. of the glycerine solution mentioned above was added 10 c.c. of normal potassium hydroxide in alcohol and 10 c.c. additional alcohol (95%). These were shaken together thoroughly and the resulting solution remained clear and limpid indefinitely. After several days standing this could be diluted with water without precipitating nickel hydroxide, and, after dialyzing, a clear gelatinous mass of the hydroxide remained.

2. By carefully warming it was found that 100 c.c. of glycerine would dissolve 6.7 grams of nickel acetate, although some acetic acid was lost in the process. To 16 c.c. of this solution was added 6 c.c. of normal potassium hydroxide in alcohol and 2 c.c. of distilled water. When such a mixture does not gelatinize, which occurs about two-thirds of the time, after standing several days it can be diluted with water without producing a precipitate. When this is dialyzed a clear semigelatinous mass of nickel hydroxide remains.

The most rapid method of obtaining a colloidal solution of nickel hydroxide is that given in the former paper (p. 731). Additional proof has been obtained that the peptization of the hydroxide is due to small amounts of potassium chloride remaining in the solution. Nickel hydroxide was prepared as described there, but was settled by means of a centrifuge, and by this means

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[1] Tower and Cooke: J. Phys. Chem. 26, 733 (1922).

the amount of potassium chloride remaining mixed with the precipitate could be regulated very exactly. After settling by this means additional distilled water was added, the precipitate settled again by centrifuge, and this continued as long as desired. The precipitate could be washed fifteen times this way in an hour and a half, which would remove the potassium chloride practically completely. Nickel hydroxide prepared in this manner and left standing in distilled water over night would not go into colloidal solution. Neither would it, if it were washed by centrifuge only two or three times, for in this case too much potassium chloride was present. However, if it were washed this way six or seven times and allowed to stand in contact with distilled water it would pass into colloidal solution in a few hours.

To see whether nickel hydroxide, as it is ordinarily precipitated from solutions as an apple-green gelatinous mass is really $Ni(OH)_2$ or is NiO with adsorbed water, a method used by van Bemmelen[1] in investigating gelatinous silica and ferric oxide has been employed. Samples of nickel hydroxide obtained by precipitating both from hot and from cold solutions were used. These were air-dried, pulverized, and left in a vacuum desiccator over sulfuric acid of increasing concentration until the weight became constant. The temperature of the room in which the desiccation was carried on was maintained at 20° ±1°. The samples were kept on watch glasses with ground edges, and during weighing this was covered with a second one clamped tightly to it in order to prevent absorption of moisture from the air. Weighings were made every day and continued until the weight became constant. The sulfuric acid in the desiccator was then replaced by the next more concentrated solution, and the process repeated until finally the weight became constant over the 98% acid.

Sulphuric Acid in Desiccator			Tension of Aqueous Vapor at 20°			
Composition	Percentage	Density at 20°			Sample 1. Grams	Sample 2. Grams
			mm.	Orig. Wt.	2.3902	2.3020
H_2SO_4 $5H_2O$	52.13	1.416	5.79	After 2 wks	2.3808	2.2972
H_2SO_4 $4H_2O$	57.65	1.473	3.73	After 3 wks	2.3221	2.2465
H_2SO_4 $3H_2O$	64.47	1.547	2.24	After 3 wks	2.2516	2.1843
H_2SO_4 $2H_2O$	73.13	1.647	0.85	After 3 wks	2.1895	2.1251
H_2SO_4 H_2O	84.48	1.774	0.15	After 3 wks	2.1858	2.1217
H_2SO_4	98	1.836	–	After 2 wks	2.1845	2.1209

In the accompanying table the first three columns give the composition and density of the sulfuric acid used, the fourth column gives the tension of aqueous vapor over the acid, and the fifth and sixth columns give the weights of the samples of nickel hydroxide after constancy had been attained over the corresponding solution of sulfuric acid.

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[1] Z. anorg. Chem., **13**, 315 (1897)

Sample 1 was prepared from hot solutions and sample 2 from cold solutions. No difference was noticed in their conduct, except that sample 2 was a little more hygroscopic after it was dry. The loss of water in both samples was fairly regular and shows no probability of the existence of a hydrate over the range investigated. The composition of the final material was determined by estimating the nickel electrolytically with the following results:

	Sample 1	Sample 2	Theoretical for $Ni(OH)_2$
Percentage found	63.14	63.08	63.30

The substance dried to constant weight in a vacuum over concentrated sulfuric acid therefore appears to be $Ni(OH)_2$ and not NiO or any intermediate hydrate.

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NOTE ON SIMPLICITY OF MECHANISM OF REACTION AS ONE OF THE FACTORS CONDITIONING CATALYSIS

BY E. R. BULLOCK[1]

Increase of velocity of reaction between a metal and a reducible substance in aqueous solution by a salt of another metal is of somewhat frequent occurrence. When the second metal is more noble than the first it becomes deposited on the latter, and the increase of reaction velocity can be electrically explained. When, however, the second metal is less noble than the first, this explanation is precluded, and the phenomenon represents a case of catalysis.

In a number of photographic after-processes (Ozobrome, Kodachrome, bromoil, etc.) a solution containing a dichromate and a bromide, with other substances, is used for the purpose of converting a silver image into silver bromide together with a chromium compound which alters the properties of the gelatine in a desired manner. The reaction between silver in gelatine and a solution of potassium dichromate and bromide slightly acidified with acetic acid is impractically slow but is greatly quickened by the addition of potassium ferricyanide or copper sulphate, which is found unaltered in the solution after use, and has therefore acted as a catalyzer. It seems probable that a clue to the explanation of the effect may be found in a principle of simplicity. Considering the case of the reaction between silver and the bleach solution of the Kodachrome process, *viz.*,

Potassium bromide	2.8 g.
Alum (potassium, aluminum)	2.5 g.
Potassium dichromate	1.9 g.
Potassium ferricyanide	1.9 g.
Acetic acid (glacial)	0.5 cc.
Water to make	100.0 cc.

in the absence of the potassium ferricyanide the net result of the reactions is represented by the equation:—

$$6Ag+6CrO_3+6KBr=6AgBr+Cr_2CrO_6+3K_2CrO_4,$$

but the initial ionic reaction is that between silver and sexavalent chromium, $3\ Ag+Cr^{++++++}=3\ Ag^{+}+Cr^{+++}$, in which three atoms of silver participate. The equation for the reaction between silver and ferricyanide, $Ag+Fe(CN)_6^{---}=Ag^{+}+Fe(CN)_6^{----}$, requires only one atom of silver and it thus seems intelligible that, notwithstanding the smaller potential difference, the velocity is greater in the reaction between silver and ferricyanide than in that between silver and dichromate. Copper sulphate acts likewise, the initial phase of the catalyzed reaction being $Ag+Cu^{++}=Ag^{+}+Cu^{+}$

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[1] Communication No. 186 from the Research Laboratory of the Eastman Kodak Company.

A search through the 70-page subject index of Woker's "Die Katalyse" for further examples of catalyzed reactions of this type disclosed only the case of the increase of velocity of the reaction between zinc and a dilute solution of potassium permanganate and sulphuric acid by the addition of a trace of pure nitric acid.[1] This fact, which can be readily confirmed, may be explained on the basis of the relative simplicity of the reaction $Zn + N^{V} = Zn^{++} + N^{III}$. As a further test of the validity of the view that, other conditions being the same, the reaction velocity is greater the fewer atoms of the metal participate in the initial stage, the effect of ferric sulphate or nitrate on the reaction between silver and bromic acid was considered. In this case, six atoms of silver are required in the direct reaction between silver and bromic acid, and only one atom in the first stage (between silver and ferric ion) of the indirect, catalyzed reaction, and from this, together with the fact that ferrous ion is re-oxidized to ferric with immeasurable rapidity by bromic acid in solution, it appeared very probable that a ferric salt would catalyze the reaction between silver and bromic acid.

Experimental. A solution was prepared containing potassium bromate and sulphuric acid equivalent to N/20 $HBrO_3$, and the action of this solution upon strips from a roll of positive cinematograph film containing a series of uniformly exposed and developed images from one and the same negative image, after prolonged washing in distilled water, was observed, and compared with the simultaneous action of a solution containing in addition N/10,000 ferric ammonium sulphate or ferric nitrate. The rate of action of the latter solutions, as followed by the "bleaching" of the silver image, was the same and in each case several times as fast as that of the solution to which no ferric salt had been added. In order to avoid any complication due to tanning of the gelatine through liberation of bromine from traces of soluble bromides, the solutions were then treated with a little silver nitrate to produce the maximum slight opalescence, and a bath of dilute silver nitrate solution was interposed in the distilled water washing of the film strips; under these conditions the reaction velocity was increased in all cases; but the iron-containing solutions still bleached the image several times as fast as did the iron-free solution. Addition of silver nitrate in increasing amounts in excess of the amount required to combine with the trace of bromide failed to show any further increase in reaction velocity, and it seems probable therefore that the silver nitrate by combining with bromide prevented the inhibiting effect of the liberation of a trace of bromine. Addition of sulphuric acid to the N/20 bromic acid to a concentration ten times that which would be produced by the complete hydrolysis of N/10,000 ferric ammonium sulphate did not produce any observable increase in reaction velocity, and it is therefore concluded that it is to the ferric ion alone that the observed catalysis must be ascribed. To observe the effect in the absence of gelatine, 25 cc. of the iron-free and 25 cc. of the iron-

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[1] DeKoninck: "Lehrbuch der qualitativen und quantitativen chemischen Anaylse," 1, 517 (1904).

containing bromic acid were left alternately for 2 hours in a silver crucible at 20° C., and the loss of weight after washing in this sulphate solution, noted: the mean loss in the former case was 0.4 mg. and in the latter 4.5 mg., showing a velocity increase of the order of ten times, due to the presence of N/10,000 ferric sulphate in N/20 bromic acid.

Conclusion. The catalysis of the reaction between silver and potassium dichromate in aqueous solution by potassium ferricyanide or copper sulphate, that between zinc and potassium permanganate with sulphuric acid in dilute solution by nitric acid, and that between silver and bromic acid by ferric sulphate may be explained in part by the consideration that the first stage of the indirect (catalyzed) reaction is of greater simplicity, as regards the number of atoms of the metal participating, than the direct reaction. Further instances of systems in which catalysis may be expected on this consideration should however be sought for and tested before the suggested principle is accepted as valid.

April 18, 1923.
Rochester, N. Y.

NEW BOOKS

Surface Tension and Surface Energy. *By R. S. Willows and E. Hatschek. Third edition. 8×5 cm; pp. viii+136. Philadelphia: P. Blakiston's Son and Co., 1923. Price $2.00.*—"The present edition of this small book has been enlarged so as to include an account of the work recently done on the properties of thin films, polarised molecules, and boundary lubrication. This work points to possible connections between surface tension and other chemical and physical properties of liquids, and in addition opens up many fascinating avenues for research. If the account here given leads readers to refer to the original papers, its object will have been gained. Other small additions and changes have also been made."

The results obtained by using the Eötvos-Ramsay-Shields formula do not "agree in all cases with those following from Walden's formula: thus, benzene is associated according to Walden and non-associated according to Ramsay. The discrepancy is particularly striking in the case of sulphuric acid, which has aggregates consisting of as many as thirty-two molecules according to Ramsay, while Walden finds aggregates of two molecules only," p. 42.

"In the preceding pages we have availed ourselves of only one of the theories of surface tension, that of Laplace. It has led us directly to recognise an important property of liquids—their cohesion or intrinsic pressure—and has enabled us to establish several theoretical relations between surface tension and other constants. It is, however, incomplete in one particular, inasmuch as it assumes that there is a perfectly sharp line of demarcation between the two media bounding the surface, for instance, between liquid and air. We need not discuss whether such an abrupt transition is intrinsically probable, as there is a large amount of evidence, principally optical, to show that there is a gradual change in density and in other properties from those of one medium to those of the other. It can, for instance, be shown that plane polarised light should be reflected again as plane polarised light, and, therefore, be capable of being completely extinguished by a Nicol prism, if the transition from one medium to the other were abrupt. Actually this is never the case with an old surface, especially in the case of metals, but the light is always elliptically polarised. With perfectly fresh surfaces this is not the case; thus Lord Rayleigh showed that the ellipticity nearly disappeared at the boundary air-water if the surface of the latter was constantly renewed, and Drude proved its absence from the surface of a freshly split crystal.

"To account for the phenomenon it is necessary to assume a film of different density on the surface, of which the order of magnitude of the thickness can be calculated, approximately; it is about 10^{-7} cm. for the surface crown glass-air. We shall have occasion to refer to this surface film again. There is also other experimental evidence for its existence; it is, for instance, a common experience in vacuum tube work that, after first pumping down and allowing the apparatus to stand, the pressure rises again owing to gas coming off the walls. Baly and Ramsay found it nearly impossible to test Boyle's law at very low pressures owing to this released gas, the amount of which varies with temperature and pressure," p. 48.

"In view of the fundamental importance of the Gibbs-Thomson formula, and the magnitude of the discrepancies between the figures calculated from it and the experimental results, it is of obvious interest to inquire to what causes the deviations may be due. The first point to be noticed is that the complex substances which exhibit them most markedly form, at least at higher concentrations, colloidal and not true solutions. It is, therefore, very probable that they may form gelatinous or semi-solid skins on the adsorbent surface, in which the concentration may be very great. There is a considerable amount of evidence to support this view. Thus Lewis finds that, if the thickness of the surface layer be taken as equal to the radius of molecular attraction, say 2×10^{-7} cms., and the concentration calculated from the observed adsorption, it is found, for instance, for methyl orange, to be about 39%, whereas the solubility of the substance is only about 0.078%. The surface layer, therefore, cannot possibly consist of a more concentrated solution of the dye, which is the only case that can be dealt with theoretically, but must be formed of a semi-solid deposit," p. 78.

"It is, however, by no means certain that the results obtained by the 'waterfall-electrification' method are comparable with those obtained by cataphoresis, or, in other words, that the origin of the double layer is the same in both cases. Thus, in experiments according to Quincke's method made by one of the authors, fuchsin did not reverse the charge on the air bubble even in concentrations a thousand times greater than those found effective by Rohde. Similarly discordant and very important results are obtained by McTaggart, who investigates the cataphoresis of a gas bubble by an improved method. The bubble is placed in the axis of a wide rotating tube filled with liquid and is therefore as freely movable as the particles in the U-tube employed for examining colloidal solutions. He finds that air bubbles are negatively charged in distilled water and travel with a velocity, independent of their size within limits, of about 4×10^{-4} cms. per second in a field of 1 volt/cm. This is in very good agreement with the behaviour of colloidal particles in the same conditions. On the other hand, he finds that in this arrangement hydrogen bubbles are, like air, negatively charged, whereas in waterfall experiments this gas is positive against water. The effect of various cations was found to be similar to that on colloidal particles, ions of high valency having a much greater effect in neutralising and eventually reversing the charge on the bubble, while exhibiting—as in their action on sols—specific peculiarities.

"In a further series of experiments McTaggart investigated the electric state of the air bubble in mixtures of water and of several alcohols, and the results obtained are of particular interest, as showing a definite connection between surface tension and electric charge. In the pure alcohols no cataphoresis could be observed. In mixtures of the alcohols and water the velocity of the bubble decreased with increasing alcohol content, and this decrease in velocity—and therefore in electric charge—was the greater the more the alcohol lowered the surface tension of water. The electric charge was therefore reduced by increasing adsorption of alcohol at the surface air-solution, and it is reasonable to assume that with an increased ratio of alcohol in the surface layer, ions would be displaced out of that layer, with a corresponding decrease in the total charge. A further very striking fact was observed; if the size of an air bubble in the water-alcohol mixture was gradually reduced, the velocity, and therefore the charge, increased, approximately more and more to that in pure water. To explain this it is necessary to assume that with decreasing diameter and the consequent change in surface tension the adsorption of alcohol decreases, or, in other words, the percentage of water in the surface layer, and with it that of ions increases. This would be analogous to the change in vapour pressure with the curvature of the surface, which has been fully discussed in a previous chapter. It is possible that the polar molecules of alcohol have greater difficulty in arranging themselves on the highly curved surface of the smaller bubble.

"On the whole McTaggart's experiments, as far as they are at present capable of interpretation, strongly support the view that the double layer is largely or entirely due to the ordinary adsorption of ions," p. 104.

Wilder D. Bancroft

Kolloide in der Technik. *By Raphael E. Liesegang. 22×15 cm; pp. 161. Dresden and Leipzig: Theodor Steinkopff, 1923. Price: 78 cts.*—This volume aims to give the recent developments in the colloid chemistry of the following subjects: glue and gelatine; other adhesives; protecting colloids; plastic masses; tanning; soap; oils and resins; rubber; paper; textiles and dyeing; metals; ceramics; foods; photography. Although necessarily much condensed, the text is quite satisfactory and no one can read the volume without finding a number of new and interesting things.

Glue is properly a mixture of gelatine and gelatose. Gelatine has a high jelling and a low adhesive power . Glue has a very high adhesive power and only a slight tendency to form jellies. When the splitting of the gelatine has gone further, both the adhesive and the jelling powers become zero, p. 7.

Michaelis has found that the hydrogen ion concentration at which casein precipitates is affected by the presence of salts, a strongly adsorbed cation being equivalent to an acid and a strongly adsorbed anion to an alkali. With rubidium chloride and sodium acetate the two ions are apparently adsorbed so nearly equally that these two salts have no effect on the point for optimum precipitation, p. 22.

Dilute solutions of olive oil and of tallow soaps are not readily affected by electrolytes, while solutions of cocoanut oil and palmnut oil soaps are very sensitive to electrolytes, p. 43. The tendency of soap solutions to foam varies very much with the nature of the soap. The author points out that potassium soaps give smaller and more stable bubbles than sodium soaps and are therefore used in shaving soaps; but he does not explain why, p. 48. It is admitted quite frankly, p. 50, that the theory of washing with soap is not yet in an absolutely satisfactory form. Attention is drawn, p. 56,—though not under washing—to the extraordinary emulsifying power of water-glass solutions for vegetable and animal oils, p. 56.

The discussion of the vulcanization of rubber, p. 71, is distinctly unsatisfactory, the author evidently not having understood Spence's work at all. Under coagulation of latex, p. 68, one would have liked to have seen something more about the relation between the size of the globules and precipitation by centrifuging. There is some confusion, perhaps naturally, in the discussion of the rosin sizing of paper, p. 81. For the same reason the paragraph on mordants, p. 91, is not so good as it might be. In fact the whole chapter on dyeing is not up to standard.

Three pages are devoted to addition agents in electroplating, p. 106. There is a very interesting discussion, p. 109, on the cause of spots in slip-casting. Under food products we find a discussion of the rising of cream, p. 120; of the making of butter, p. 121; and of whipped cream. There are two pages on bread, p. 124, and one on beer, this latter topic coming for some unknown reason between bread and vitamines, p. 127. The book closes with nineteen pages on photography.

Wilder D. Bancroft

The Principles of Organic Chemistry. *By James F. Norris. Second edition. 21×15 cm; pp. xi+631. New York: McGraw-Hill Book Company, 1922. Price: $3.00.* The first edition was reviewed over ten years ago (**17**, 280). In the preface to this edition the author says: "The development which has taken place in organic chemistry since this book was published has made it necessary to prepare a new edition. This development has been marked on both the theoretical and the practical sides of the subject. While the advances in the pure science have been largely of such a character that they should not be included in an elementary textbook, the development of industrial organic chemistry has tended to vitalize the subject and to arouse the interest of the beginner. As the result of the recent war there was an increased demand for a large number of organic compounds of industrial importance. The search for new methods of preparing these substances on the large scale led to the utilization of reactions which were formerly of theoretical interest only, or to the application of newer methods such as those of catalysis and electro-chemistry. These new industrial processes have been emphasized as fully as is consistent with the scope of the book.

"The growth of the dyestuff industry in America made it desirable to broaden to some extent the treatment of the aromatic compounds and to include brief descriptions of the more important intermediates and of the sulphur and vat dyes. The increasing use of the organic derivatives of mercury and of arsenic in combating disease made it necessary to introduce an elementary consideration of the general reactions underlying the preparation of such compounds.

"The renewed interest in the application of organic compounds in warfare has led to the description of the more important war gases and the new explosives. The consideration of the chemistry of fats, carbohydrates, and proteins has been extended to include the physiological aspects of the subject.

"The additions to the text in the field of the pure science have been limited in number. It is the opinion of the author that the newer theories, such, for example, as the interpretation of the reactions of organic compounds by means of the electronic conception of matter, should not be included in the first elementary presentation of the subject, with the resultant exclusion of important theoretical material based on a more substantial experimental foundation. In this edition the theory of partial valence and the relation between chemical structure and color are briefly discussed. There is given, also, an account of the recent work on the structure of tannins and the coloring matter of flowers."

The fact that over twenty thousand copies have been printed shows that the author has found a large public and is the best proof that this is the kind of book that a great many people want. As one glances through the volume, one is not surprised at its popularity.

Wilder D. Bancroft

The Phase Rule and its Applications. *By Alexander Findlay. Fifth edition. 22×15 cm; pp. xvi+298. New York and London. Longmans, Green and Co., 1923. Price: $3.50.*—In the preface to the new edition, the author says:—"The increasing attention which has been paid in recent years to heterogeneous equilibria and the re-investigation of some of the important problems connected therewith, have necessitated a complete revision and re-writing of certain sections and the addition of much new matter. The sections on sulphur and phosphorus, for example, have been re-written, the attention being directed more especially to the pseudo-binary nature of these systems. The section on iron-carbon alloys, also, has been revised in the light of recent work and, as far as space would permit, the most important work on four-component systems and the sales of the Stassfurt deposits has been discussed. The opportunity has also been taken of explaining more fully the graphical methods of representation of multi-component systems, and more especially the graphical methods suggested by Jänecke which are now very widely employed. The importance of the Phase Rule in the study of mineralogical problems has been emphasized by a discussion more especially, of the conditions of formation of the calcium aluminum silicates. It is hoped that the considerable extension of the work which has thereby been brought about and the addition of twenty-four new diagrams will add to the usefulness of the book." This is the standard book on the phase rule. There is nothing else that can come anywhere near it. It should be—and probably is—used as the text-book everywhere that the subject is taught and that is now everywhere. We rejoice that Findlay has brought this book up to date. Owing to the war it has been eight years since a new edition has appeared.

Wilder D. Bancroft

Les Progrès de la métallurgie du Cuivre. *By Auguste Conduché. 20×13 cm. pp. xv+254. Paris: Masson and Cie, 1922. Price: 14 francs.*—This is the second volume in the second series of the Encyclopédie Léauté. The first part of the book deals with: the properties of copper; the copper alloys; the properties of the copper salts; the copper minerals; and the output of copper. The second part deals with the treatment of the ores and the chapters are entitled: roasting the ore; making the matte; pyritic fusion; making matte in a reverberatory furnace; conversion of the matte into raw copper; metallurgy of the complex ores; extraction of copper by the wet way; refining copper in the furnace and electrolytically.

The author suggests, p. 23, that the beneficial effect of copper in preventing atmospheric corrosion of steel may be due to the formation of cuprous sulphide. Interesting also is the statement, ascribed to Guillet, p. 20, that the solid solutions of malleable metals like silver and copper are also malleable. The data in regard to electrolytic refining of copper are taken mostly from the Great Falls plant of the Anaconda Company.

Wilder D. Bancroft

A Dictionary of Applied Physics. *Edited by Sir Richard Glazebrook. Vol. II. 23×17 cm; pp. vii+1104. New York and London: The Macmillan Co., 1922. Price $15.00 per volume.* This is practically a treatise on electricity arranged alphabetically instead of systematically. Among the important headings are: alternating current instruments and measurements; arc lamps; primary and secondary batteries; electrical capacity; electrolytic condensers; manufacture of carbons for arcs; dielectrics; direct current indicating instruments; systems of electrical measurements; electrolysis and electrolytic conduction; technical applications of electrolysis; electromagnet; electron theory; electrons and the discharge tube; galvanometers; incandescence lamps; inductance; magnetic measurements; modern theories of magnetism; photoelectricity; piezo-electricity; positive rays; potentiometer; radio-frequency measurements; resistance; stray current electrolysis; switch gear; telegraph; telephone; thermionics; transformers; units of electrical measurements; watt-hour meters; wireless telegraphy and telephony; X-rays.

"An ordinary carbon arc burning in air will always hiss when the current density in the positive carbon exceeds the critical value for that particular carbon. Hissing will begin below this value with a short arc. It may also start if a sudden increase of current causes the arc stream to expand beyond the rim of the crater, or if one of the carbons is moved sideways or the arc is blown sideways.

"When hissing starts there is always a sudden fall in the arc voltage, and this fall practically all occurs near the positive crater region. Mrs. Ayrton gives the results of a long series of tests on hissing arcs. Her conclusions are that the hissing and the fall of potential are due to the oxygen of the air getting to the crater surface, because an arc will not hiss if surrounded with nitrogen or carbon dioxide. The explanation suggested for the quick movements is that air first combines with the carbon on part of the crater surface, then the products of combustion temporarily shield the surface but afterwards disperse, and a fresh supply of air rushing in the action is repeated," p. 48.

"The modern negative carbon for searchlights and cinema projectors is made small in diameter and has also special means for keeping the current-path central. It is provided with a high conductivity core of hard carbon and the core is heavily coated with copper. This core is virtually the electrode proper—the use of the outer shell is chiefly to support the core and to protect it from oxidation. The positive carbon is also made small in diameter, the current density being increased until it is as near the hissing point as is practical," p. 49.

"Arcs burning in vacuum or inert gases are of no use for illumination, mainly because it is necessary to carry away from the arc all the material which is evaporated. If any of it condenses on the carbon unsteadiness results. Even in air a short arc will "mushroom"—that is, carbon will build up on the negative, destroy its symmetrical shape, and cause unsteadiness, besides blocking the light. However, in "enclosed" lamps and lamps fitted with economisers advantage is taken of gases less active than pure air. In enclosed lamps the oxygen becomes exhausted by combustion of the carbon, also the heat in the enclosure rarefies the gases. The inlet for fresh air and the size of the globe are adjusted until the burning away of the carbon is just fast enough to keep the ends clean. The carbons become praccally flat on the burning ends and the arc is continually moving about burning each part in turn—the area of the carbon being much greater than the area of the arc.

"When flame carbons are used in enclosed lamps it is necessary to deposit the fumes on surfaces other than the enclosing globe. This is done in several ways, but all depend on convection currents carrying the gases into additional chambers and over large cool surfaces on which the fumes are deposited, the gases returning to the globe after they have been clarified. It is necessary to keep the globe hot to prevent condensation on its surface, and therefore it is generally surrounded by another globe which keeps the cool outer air away from the inner globe," p. 51.

"The action of ozone (produced by high-tension static discharges) on rubber dielectrics exposed thereto at cable ends trimmed of their coverings to prevent surface leakage, furnishes a remarkable instance of an abstruse kind of deterioration, which often appears in the form of splits or cracks. The writer has demonstrated that this only occurs when the rubber is under tension, as on the outer periphery of a bend, and not when the cable end is straight and therefore free from tensile stress at any part of its surface. In the former case the defect may occur within a few minutes of the exposure of the rubber to the gas, whereas practically no deterioration occurs—as judged by the effect of heat tests on the rubber—in the latter after long exposure.

"A point of interest in this connection is that vulcanised bitumen is quite immune from this peculiar effect, but admixture of a very small percentage of rubber with it destroys this immunity. The cause of this phenomenon has not been determined," p. 100.

"Experience shows that solid laying in bitumen-filled troughs is not a preventive against electrolytic action on the cable, in fact under some circumstances it may aggravate it, because the virtual electrode area is very restricted, and therefore the current density is likely to be high and the corrosion effects correspondingly severe. Again, for similar reasons, metal-sheathed wiring in damp situations in buildings, particularly if run in wood casing, is liable to be badly attacked unless special precautions are taken. These precautions consist in metallically bonding all sheathings together, and earthing them at the source of supply. Intermediate earth plates may be necessary in some cases where the electrolytic survey indicates that current would enter or leave the sheath, so that it can do so by a metallic path. Care has to be taken, however, to avoid inviting vagrant currents on to the cable sheaths.

"In principle, the whole matter amounts to short circuiting all the potential electrolytic paths so that any current flowing from or to sheathings passes along metallic conductors instead of by electrolytic paths.

"This general principle, first enunciated by the writer many years ago, in opposition to the principle then being largely supported of segregating the sheaths of adjacent lengths of cable, together with the Board of Trade restrictions bearing on maximum earth return voltages, has rendered electrolytic troubles on large networks in this country almost negligible, so far as vagrant currents from external sources (such as electric tramways) are concerned. It has also permitted the free use of metal-sheathed wiring in buildings, which for many years was under an inexplicable cloud owing to troubles which were—though usually attributed to other causes—due to electrolytic action arising from leakage currents from the wires and cables themselves. At the present time the strictest attention is paid to continuity bonding and earthing in metal-sheathed wiring systems; in fact the chief features of most of the special systems now in vogue bear on the matter of efficient and permanent bonding," p. 100.

"When passages exist in a negative cable—even of a capillary order—water is forced along them for considerable distances and up to appreciable pressures by the endosmotic effect. In rubber cables, for instance, blisters full of water are sometimes found to be produced, and on cutting a badly affected cable, water will sometimes spurt for a considerable distance," p. 101.

"Condensers of very large capacity can be constructed without difficulty of metal plates immersed in suitable electrolyte. The metal used must belong to the class known as 'valve metals', such as aluminum, magnesium, or tantalum, which have the property, when made the anode in certain electrolytes, of forming on their surface a thin, porous, adhesive layer separated from the actual metal by a thinner layer of gas having an extremely high resistance, which, even with a very small current, allows a high voltage to be maintained. If the applied (direct current) voltage is raised above a certain maximum, which depends on the nature of the electrolyte used, the gas layer breaks down and numerous discharges with sparking occur. For example, for aluminum in solution of sodium sulphate the maximum is 40 volts, whereas in solution of ammonium phosphate it is 460 volts. With aluminum one of the best electrolytes is a saturated solution of ammonium borate $(NH_4)HB_2O_4$. Two sets of plates are immersed in this, care being taken to insulate the conductors as they pass out of the liquid surface; by the application of (say) 100 volts (direct current) for several days to the two sets in parallel against a platinum cathode, the plates are 'formed.' The two sets are then separated and form an electrolytic condenser which can be used with alternating voltages as high as 90 volts, and with this voltage it shows a power factor of about 0.05," p. 123.

Arc carbons are usually made from a mixture of lamp-black and ground petroleum coke or pitch coke held together by a suitable binder such as pitch or tar. The highest grade carbons may contain up to eighty percent of lamp-black, while lower grade carbons may run as low as twenty percent in lamp-black. The rods are made by pressing through a die. Where cored carbons are required, the hole is formed by means of a suitable steel needle in the die. Pressures of five tons to the square inch are used. The carbon rods are calcined slowly up to a temperature of 1200°. The cored carbons then have to have the core canal filled. "The cored carbons which are used in ordinary open type or enclosed type lamps, for the so-called pure carbon arc, have the core canal filled with a mixture of carbon and potassium silicate. The carbon is in the form of a very fine powder, which is mixed with a solution of potassium silicate until it has the consistency of a fairly thick cream. This mixture is then injected into the core canal, which it completely fills, and the carbon is then dried at a temperature sufficiently high to drive off all the moisture in the coring mixture. The core is then in the form of a dry powder held together in its place by the dry silicate of potash. The function of the silicate of potash is not only to act as a binding material, but to lower the resistance of the arc and, as has been explained elsewhere, to centralise the arc at the end of the carbon. For flame arcs, suitable chemicals are introduced in the form of powder into the coring mixture; calcium fluoride is used when a yellow flame arc is required: cerium fluoride for a white flame arc: other compounds can be used for producing special colours," p. 145.

"The original flame carbon had the flame-producing material distributed throughout the mass of the carbon, the ingredients being introduced into the original mixing before pressing. Experience showed, however, that in open type flame lamps better results could be obtained by concentrating the ingredients in the core. In recent years, however, the development of the enclosed type flame lamp, where the carbons burn in an enclosure from which the air is largely excluded, have necessitated the manufacture of a flame carbon in which the ingredients are introduced into the original mixture, and which is therefore homogeneous throughout its section. Carbons burning under these conditions naturally do not taper to a point but burn with a practically flat end, and it is therefore necessary for the flame-producing material to be evenly distributed instead of concentrated in a central core. Open type lamps have also been recently developed for which the most suitable type of carbon is one consisting of an outer shell of pure carbon with an inner solid carbon containing flame-producing material. To manufacture such carbons, the two parts are prepared separately and the inner rod inserted in the shell, either before or after baking, and suitably cemented to it," p. 146.

The sections on systems of electrical measurements and on electrical units are surprisingly good. The reviewer was interested also in the section on photoelectricity. The pages on positive rays were written by Aston and those on electron theory and spectrum analysis by the elder Bragg. Jewett wrote the section on telephony and Richardson the one on thermionics.

The editor has had the best of assistance and the volume is one to be proud of.

Wilder D. Bancroft

Absorption of Nitrous Gases. *By H. W. Webb. 23×15 cm; pp. viii 372. New York and London: Longmans, Green and Co., 1923. Price: $8.50.* "In peace and war alike the supply of fixed nitrogen is of vital importance to the exestence of the nation. In almost all processes for the fixation of nitrogen the production of oxides of nitrogen is one of the fundamental intermediate stages. It cannot be said at the present time, however, that the problem of the technical utilization of nitrous gases (which are usually largely diluted with air) has met with a satisfactory solution. The enormous number of patents relating to the process which appear each year would seem to be sufficient evidence of the truth of this statement. It is the common practice at the present time to absorb the nitrous gases in water with the production of dilute nitric acid, which acid is either concentrated or converted into solid nitrates. In this country, where nitrous gases are produced (in the majority of cases) only as by-products, the chemical principles underlying the process have not been studied to a very great extent, and it is very often the case that the absorption process is conducted on rule-of-thumb methods. While the loss of fixed nitrogen in such plants may not be a very serious factor in the series of industrial operations with which it is connected, the same view cannot possibly be held when the recovery of the nitrous gases is one of the main objects of those industrial operations. Furthermore, it has long been evident that we, in this country, must ultimately adopt some process for the fixation of nitrogen, in view of the fact that we import nearly all our fertilizers.

"With these points in view, the author has endeavoured to discuss the absorption of nitrous gases in water, both from a theoretical and an industrial standpoint. The most important types of absorption processes, other than water absorption, which have been developed are also considered, and an attempt has been made to classify and compare them, in order to survey the present position, so far as this particular branch of the nitrogen-fixation industry is concerned. It has also been thought necessary to review briefly the methods available for the commercial utilization of the dilute nitric acid normally obtained from the water-absorption process."

The chapters are entitled: oxides and oxyacids of nitrogen; theoretical problems of absorption; construction of absorption towers; filling material for absorption towers; gas circulation and measurement; the handling of nitric acid in the absorption system; production of concentrated nitric acid; production of synthetic nitrates and nitrites; analytical control.

In the introductory chapter is the statement, p. 5, that the first oxidation product of nitrogen at high temperatures is nitrous oxide and that this can be isolated in fair yield. There is a good discussion of the action of nitric acid on metals, pp. 64-87, though the reviewer would have welcomed laying more emphasis on what we do not know.

"If alkaline liquids are used as absorbents of nitrous gases, large quantities of liquid have to be evaporated. If, on the other hand, dry metallic oxides such as zinc oxide or aluminum oxides are used, these are so weakly basic that their absorbing effect is very small. In this connection Halvorsen proposes to use as the absorbent a mixture of caustic soda and oxides of zinc, or iron, or aluminum, in the form of briquettes. . . . This suggestion is theoretically attractive for use with very dilute nitrous gases. So far as can be ascertained, however, it has not yet been applied to large-scale practice, and it is probable, as is so often the case, that the practical difficulties in the way of the process outlined have outweighed any theoretical advantages. One of the chief troubles in all these processes in which solid oxides and salts are used as absorbents is caused by the presence of moisture in the nitrous gases being absorbed. Equilibria are set up, and the reaction is hence incomplete and the process inefficient. It is very difficult to see that such modifications of the absorption process are economical, since it would seem that any saving in the initial cost of tower construction would be more than compensated by the operation costs of such concentration processes. Furthermore, it appears to be cheaper to treat the products of absorption of dilute nitrous gases to obtain the final concentrated product required, rather than carry out any concentration process on the nitrous gases themselves. The position would depend to some extent, however, on the available market for the final product of absorption," p. 121.

"The concentration of nitrous gases by liquefaction has been frequently suggested for consideration in recent years as an adjunct to water-absorption systems for nitrous gases, and particularly in plants where moderate concentrations of nitrogen are available, i.e. in which liquefaction can be obtained quickly and completely by cooling alone without resort to increased pressures," p. 122. "There are three important disadvantages to such liquefaction processes.

"1. Unless very low temperatures and very high pressures are used it will not be possible to liquefy the whole of the nitrogen oxides from a dilute mixture with air, and operation, even at the temperature of liquid air, would appear to be uneconomical.

"In this connection some figures communicated to the author on gases from ammonia oxidation, containing about 7 percent of nitrogen tetroxide (as NO_2) mixed with air, showed that 60 percent of the tetroxide could be liquefied at -50°C at atmospheric pressures, and 90 percent at -80°C. This indicates that quite low temperatures would be required to secure efficient results from more dilute nitrous gases, as in the arc processes, for example.

"2. The second disadvantage of the liquefaction process lies in the fact that both nitrogen oxides and nitric acid are present in the equilibrium mixture. The complete transformation of a given quantity of liquid tetroxide into nitric acid will hence require several operations, in each of which there will be a certain loss of nitrogen oxides, both dissolved in the nitric acid and also as vapour.

"3. The third disadvantage is that the use of oxygen for oxidizing the nitrous acid formed is expensive, and, if air is used, a correspondingly greater loss occurs of nitrogen oxides mechanically carried away by the inert gas.

"Against these disadvantages, combined with the cost of compression and the production of low temperatures, must be offset the commercial value of concentrated nitric acid, containing 95 percent HNO_3, to dye-works and explosives works, and similar industries, where the mixed acids used require only a minimum percentage of water. For the general production of fertilizers, nitrites, etc., the method is obviously uneconomical," p. 126.

Under the theory of absorption, p. 144, the author says: "The difficulty of securing good distribution in a square tower is greater than with a tower of circular section, owing to the 'collecting' action of the corners in the square tower, which tend to send the liquid down in relatively large streams. The difficulty also increases with increasing diameter of the tower.

"It has been suggested that a greater efficiency of initial distribution could be obtained if the absorbent were caused to pass through a layer of fine sand, from which it would be delivered on to the packing in a large number of droplets, homogeneously distributed, owing to the capillary action of the sand particles. It seems a frutiful field of investigation to examine the possibility of utilizing capillary action for initial distribution instead of depending on carefully adjusted constant-level apparatus.

"It is sometimes the practice also to fix intermediate distribution plates at different levels in the tower. The object of this is apparently to collect up the liquid after it has fallen through a certain distance in the tower, and redistribute it, and also to give intermediate support to the packing. The procedure is, however, erroneous, since it is desirable to maintain the liquid continually as a thin film over a large area, rather than to collect it up into streams of relatively little surface. When such a device is considered necessary in a tower, it is time to consider whether the filling material is efficient so far as distribution of gas and liquid is concerned. It may be taken as a general principle that wherever a liquid absorbent is delivered on to packing material in the form of a pencil of liquid, the danger of channelling is always accentuated.

"There is little doubt that the best initial distribution of the absorbent is obtained when the liquid is sprayed or pumped into the tower under pressure, and especially if an atomizing jet is used. Whether such devices are economical in practice, however, is open to doubt. Fine sprays, for example, are quickly put out of action by grit and slime. In the case of high towers (60-80 feet) a very heavy initial pressure is required to give 10-15 lb/sq. in. necessary at the top of the tower for efficient spraying, and it is difficult to obtain acid mains which will withstand the pressure for any length of time, or even to obtain pumps or blowing eggs for nitric acid which will work satisfactorily under such conditions.

"The gravity feed, therefore, in spite of its relative inefficiency, is more reliable, and it is reliability which is a first essential in the flooding of absorption towers, since a failure in the supply means heavy losses of fixed nitrogen."

"The possibility of speeding up the absorption cycle is the motive behind a great deal of the recent research work carried out on absorption. It is obvious from what has been said before that it is the regeneration and oxidation of nitric oxide in the cycle which constitutes the main 'time reaction,' and although a number of patents suggest the removal of the regenerated NO, and its oxidation in special chambers, before admission to the tower system, the modification does not increase the capacity of the system, .

"The action of chlorine in the cycle has been specially mentioned, because it is almost invariably a constituent of the nitrous gases passing to the adsorption towers, in the pot process for nitric acid manufacture, owing to the presence of sodium chloride in the nitre used," p. 148.

It has been found that chlorine has a marked accelerating effect on the absorption, presumably owing to the intermediate formation of nitrosyl chloride. "While chlorine is not a suitable substance for the acceleration of the reaction in large-scale practice, its action suggested that the present enormous size required for absorption towers may yet be considerably reduced by development of methods in which such a principle is applied, particularly where very dilute nitrous gases have to be dealt with," p. 152.

"The type of absorption tower which has up to the present been developed is based on the assumption that the provision of oxidation and absorption space in the same tower is equivalent to the alternate absorption and subsequent reoxidation of the regenerated nitric oxide as two separate stages. In fact, it is not, as will readily be seen by a consideration of the reactions involved. The absorption of N_2O_4 molecules in water gives rise to nitrous acid and nitric acid. The former decomposes into nitric acid and nitric oxide, and the nitric oxide must subsequently be re-oxidized. It makes a great difference, however, whether or not that nitric oxide is reoxidized in the presence of liquid absorbent. The velocity of oxidation is at first rapid, and then falls off as the concentration of NO decreases. There will be formed almost instantaneously, therefore, molecules which will react effectively towards water as N_2O_3, the result being that nitrous acid is exclusively formed, and must subsequently decompose into nitric acid and nitric oxide. If however the nitric oxide originally present had been allowed to oxidize in the absence of liquid absorbent, it would, given sufficient time, have been oxidized completely to N_2O_4 molecules. This would then have given both nitric and nitrous acids on dissolving in water, and an inspection of the equations concerned will show that the amount of nitric oxide regenerated in the one case is twice that in the other. In other words, the system of allowing the regenerated nitric oxide to oxidize completely to nitrogen tetroixde doubles the capacity of the actual absorption tower. On the other hand, the time required for the complete oxidation of nitric oxide to the tetroxide is considerable, especially when the gas is dilute. The total capacity of the system would therefore be decreased if complete oxidation to N_2O_4 molecules were aimed at.

"It is quicker to allow the nitric oxide to form only N_2O_3 and a little N_2O_4, and to allow this oxidation to go on in the presence of the liquid absorbent. Although only one-third (approx.) of the resulting nitrous acid is converted into nitric acid, the cycle of reactions is so much quicker as to be advantageous over the alternative system, when the oxides of nitrogen are very dilute. This is the underlying consideration in modern absorption practice. As much oxidation as possible is allowed to go on in the towers, by using packing with high free space, but the oxidation is allowed to take place in the presence of the liquid absorbent," p. 202.

"It is a matter of common observation that the exit gases from an absorption system contain appreciable quantities of nitric acid vapour. This mist is formed to some extent even when alkaline absorbents are used in the end towers of the system, and is somewhat similar to sulphur trioxide in the difficulty of its condensation. Taylor Capps and Coolidge used a form of Cottrell precipitator to remove the mist, similar to that used in sulphuric acid manufacture, and obtained nitric acid containing 15-25 percent HNO_3. The formation of this acid must take place quite readily when the gases contain more than a certain percentage of moisture. In large-scale work the percentage of nitric acid in such acid mist has been found to be as high as 40 percent HNO_3, and the loss due to acid carried over in this way may be considerable.

"In many systems where the gases are drawn directly through a fan at the end of the system, a small amount of such mist is centrifuged out, and the quantity of 'fan drip' acid so obtained gives some idea of the total loss which may occur in this way. In present-day absorption practice, even when using a final alkaline absorbent, the efficiency obtained does not exceed 97-97.5 percent as a maximum, calculated on the basis of total fixed nitrogen recovered. The 2.5-3.0 percent loss obtained includes a handling loss of approximately 1 percent, the remainder being due to the escape of acid mist and nitric oxide from the system. Where no final alkaline absorbent is used, the efficiency of the absorption system lies between 92-95 percent if fairly concentrated nitrous gases are available. In this case the loss due to acid mist lies between 2.5-3 percent of the total output of the towers.

"The Badische Anilin und Soda Fabrik propose to dissipate a nitric mist by means of a high-tension electric discharge. Their apparatus seems to be quite similar to the Cottrell and Lodge precipitators used in this country. A recent French patent gives details of an electrical precipitation apparatus which has been used in the nitric acid industry. The potential difference used varies from 20,000-40,000 volts. The electrodes consist of aluminum plates, one of which is smooth and the other covered with asbestos fibre. It was found that with an apparatus of this type nitric acid up to 1.41 sp.gr. (65 percent HNO_3) could readily be condensed.

"It seems very probable that the application of electrical precipitation on a much wider scale to absorption practice is a very likely development in the near future," p. 212.

"As is well known, Portland cement is quite readily disintegrated by dilute or concentrated nitric acid, and, although it may be used for foundation work in many constructions, it is a potential source of danger if it is likely to come in contact with nitric acid. The behaviour of brickwork under such circumstances is well known, the lifting effect being so powerful as to destroy the security of any structure erected above it. For this reason ordinary cement and mortar should be used with great caution in the construction of plant for the treatment of nitric acid.

"The commonest type of hard-setting cement, which finds extensive application in acid manufacture, is a mixture of sodium silicate with various finely powdered siliceous materials. As long as it is resistant to acids, almost any type of siliceous material will do. Quartz, sand, asbestos, brick, etc. in a finely ground condition are all efficacious. The sodium silicate used in these cements should be of the non-vitreous type. As is well known a considerable change in the properties of sodium silicate (soluble glass) occurs on heating the solution to dryness. The product becomes relatively insoluble, and cements made from it form weak, friable masses which are readily disintegrated. In this connection it should be mentioned that R. M. Caven states that if a finely subdivided alkaline silicate is mixed with 25-38 percent of its weight of water, heated to a temperature between 70°-100°C until the mass becomes vitreous and miscible with water and is then cooled, a hard solid is obtained, which can be ground to powder, and when stirred with water readily dissolves, only about 1.5 percent remaining insoluble," p. 274.

Wilder D. Bancroft.

A DILUTION LAW FOR UNI-UNIVALENT SALTS

BY BOHDAN SZYSZKOWSKI[1]

The fact that the solutions of strong electrolytes do not obey Ostwald's dilution law, and consequently the law of mass action in respect of the equilibrium between the undissociated molecules and the ions, was apparent since the beginning of Arrhenius' theory of electrolytic dissociation. As, on the other hand, the law of mass action follows directly from Planck's characteristic thermodynamical function $\Phi\,(p,T,n_0, n_1, n_2 \ldots)$ by equating its variation at constant pressure (p) and temperature (T) to zero, under the assumption that the intrinsic energy (U) and the volume (V) are linear functions of the number of molecules $n_0, n_1, n_2 \ldots$, all hypotheses underlying the calculation of the intrinsic energy must be considered and analysed before a definite step can be taken towards improving the theory.

The numbers of molecules of different kind, $n_0, n_1, n_2 \ldots$, where suffix o applies to the solvent, suffix 1 to the undissociated molecule, and suffixes 2 and 3 to positive and negative ions, depend in the first place upon the degrees of dissociation α which are not measured directly but calculated from conductivity data or from the data of other methods, *e.g.*, from the lowering of the freezing point.

The calculation of α from the conductivity data, which are the most reliable and precise within a very wide range of concentrations, involves an arbitrary hypothesis regarding the influence of viscosity (η) upon the mobility of the ions, namely, it can be assumed that $\alpha = \lambda/\lambda_0$, or $\alpha = \lambda\eta/\lambda_0\eta_0$, or more generally $\alpha = \dfrac{\lambda f(\eta)}{\lambda_0 f(\eta_0)}$, where λ denotes the equivalent conductivity and λ_0 the equivalent conductivity at infinite dilution.

As there is no method allowing of the choice between the great variety of possible forms of the function $f(\eta)/f(\eta_0)$ the values of the degree of dissociation α remain completely undetermined, and, therefore, cannot be used as fundamental experimental data for the verification of different theories of electrolytic dissociation. This is the reason why, in spite of the greatest ingenuity displayed in that direction, no satisfactory theory explaining the anomaly of strong electrolytes has yet been forwarded.

The aim of the present paper is to show that by rejecting the classical conception of partial dissociation of strong electrolytes into ions, and by admitting Ghosh's hypothesis of complete dissociation of salts into ions independently of the concentration of their solutions, a theory of electrolytic dissociation compatible with experimental data can be established. As the first step towards the general solution of the problem, a thermodynamical theory of dissociation of strong electrolytes of uni-univalent type in aqueous solutions

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has been worked out and verified by the author. The thermodynamical method has been chosen here because it does not imply any assumption regarding the mechanism of electrolytic dissociation.

Let us suppose with Ghosh[1] that strong electrolytes are completely dissociated, and with Planck[2] that their behaviour is due to the fact that their intrinsic energy is not a linear function of the number of molecules. If we denote by U, S, C and Φ the intrinsic energy, the entropy, the Gibbs' constant of entrofy and Planck's characteristic function of the solution, further by u_0 and S_0 the intrinsic energy and the entropy of 1 gram-molecule of the solvent, by u and s the intrinsic energy and the entropy of one gram-molecule of the electrolyte, i.e. of the cation and anion jointly ($u=u_1+u_2, s=S_1+S_2$), and by n_0, $n_1=n_2$ the number of gram-molecules of the solvent and of both ions; if we take further for the definition of the concentration of ions $c_1=c_2=c=\frac{n_1}{n_0}$, and consequently calculate on this assumption the concentration of the molecules of the solvent $c_0=1-2c$; then, in case of complete dissociation, the intrinsic energy of the solution would be $U=n_0u_0+n_1u$, according to the classical conception that U is a linear function of the number of molecules, and Ghosh's hypothesis would consist in the addition of a non-linear term $U=n_0u_0+n_1[u-Gc^{1/3}]$, in which expression G denotes the constant of Ghosh. Ghosh's term, $-Gc^{1/3}$, takes account of the electrostatic field due to the ionic charges. The negative sign points to the fact that the resulting force acting between ions is attractive. As Ghosh's constant G calculated from conductivity data does not keep constant, but first rises, passes through a maximum and then falls with dilution, it is obvious that his assumption regarding the second term of the intrinsic energy, $-Gc^{1/3}$, is not correct. On the other hand, his formula does not allow either of a physical interpretation, because although the value of $u-Gc^{1/3}$, as c tends to the limit zero, approaches u in accordance with the classical theory, the fact however that dissociated ions do not recombine cannot be explained by a formula in which only attractive forces acting between ions are taken into consideration.

But if, instead of Ghosh's function, the following function for the intrinsic energy be adopted

$$U=n_0u_0+n_1[u-\beta(c^{1/3})^n+\gamma(c^{1/3})^m] \qquad (1)$$

A complete agreement between the theory of electrolytic dissociation and experimental data is reached.

In the last two terms of this formula expressing the energy of the electrostatic field account is taken of attractive $[-\beta(c^{1/3})^n]$ and repulsive $[+\gamma(c^{1/3})^m]$ forces, and as $m>n$ the repulsive forces fall more rapidly with the dilution than the attractive, and at the limit, as the concentration approached zero, first vanish the repulsive and then the attractive forces. With increasing concentration a point is reached when attractive and repulsive forces balance each other, and consequently $-\beta(c^{1/3})^n+\gamma(c^{1/3})^m=0$, for still higher concen-

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[1] Ghosh: Z. physik. Chem. 98, 211 (1921).

[2] Planck: "Vorlesungen uber Thermodynamik," §273 (1921).

trations the sum of both terms assumes a positive value, i.e. the repulsive forces predominate and do not allow to dissociated ions to recombine into neutral molecules.

By assuming with Planck[1] zero for the constant value of the pressure, $p=o$, which is equivalent to the assumption that the measurements are effected *in vacuo* instead of under atmospheric pressure, the differential equation of the entropy, $ds=\frac{du+pdV}{T}$, can be brought to a simpler form

$$ds=\frac{du}{T} \qquad (2)$$

and consequently the entropy of the ions at constant temperature will be

$$s=\frac{u}{T} \qquad (3)$$

The entropy of the solution will assume then the form

$$S=n_0s_0+n_1s+C \qquad (4)$$

where C stands for Gibbs' constant

$$C=-R(n_0\log c_0+2n_1\log c) \qquad (5)$$

If we introduce further the abbreviations φ for the terms which depend upon the temperature and the pressure but are independent of the numbers of molecules $n_0, n_1 \ldots$ ($\varphi=S-\frac{u}{T}$), Planck's characteristic function $\Phi\ (p,T,n_0, n_1=S-\frac{U}{T}$, in virtue of equations (1), (3) and (4) assumes the form

$$\Phi=n_0\varphi_0+n_1[\varphi+\frac{\beta}{T}(c^{1/3})^n\frac{\gamma}{T}(c^{1/3})]^m+C \qquad (6)$$

for the solution, and

$$\Phi^1=n_0^1\varphi_0^1 \qquad (7)$$

for the vapour or solid phase in equilibrium with the solution. The vapour or solid phase consists here obviously of the pure solvent.

The condition of equilibrium between the liquid and vapour, or liquid and solid phase will follow from the variation of $\Phi+\Phi^1$ at constant temperature and pressure

$$(d\Phi^1+d\Phi_{p,T})=o \qquad (8)$$

As the variations of the numbers of molecular *species* present are to each other in the relation

$$dn_0:dn_1:dn^1_0=-1:o:\frac{m_0}{m_0'},$$

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[1] Planck: "Vorlesungen uber Thermodynamik," § 273 (1921).

where m_0 and m^1_0 denote the molecular weights of the solvent in liquid and vapour or solid phase, equation (8) assumes the form

$$\frac{m_0}{m^1_0}\varphi_0^1-\varphi_0+n_1\frac{\beta}{T}d(c^{1/3})^n-n_1\frac{\gamma}{T}d(c^{1/3})^m+dC=0 \qquad (9)$$

or considering that $c_0=1-2c$, and

$$dC=-R\log c_0 dn_0=2Rc$$

and

$$dc=\frac{n^1}{n^2_0}dn_0=\frac{n_1}{n^2_0}$$

it follows

$$2c-\frac{n}{3}\frac{\beta}{RT}c^{1+\frac{n}{3}}+\frac{m}{3}\frac{\gamma}{RT}c^{1+\frac{m}{3}}=\frac{1}{R}\left(\frac{m_0}{m'_0}\varphi_0^1-\varphi_0\right)=\log K \qquad (10)$$

The value of log K, at constant temperature and pressure, is constant, and for the pure solvent, where $c=0$, is obviously equal to zero. On the other hand, under the same conditions the freezing or boiling point of the solution (T) is evidently equal to the freezing or boiling point of the pure solvent (T_0)

$$(\log K)_{T=T_0}=0 \qquad (11)$$

Expanding the difference $\log K-(\log K)_{T=T_0}$ with regard to temperature into Taylor's series and breaking with the first term,

$$\log K-(\log K)_{T=T_0}=\frac{d\log K}{dT}(T-T_0) \qquad (12)$$

and considering further that $\left(\frac{d\log K}{dT}\right)_P=\frac{r}{RT_0^2}$, where r is the latent heat of the transformation, we obtain from equations (10), (11) and (12) the equation

$$\frac{r}{RT_0^2}(T-T_0)=2c\left(1-\frac{n}{6}\frac{B}{RT}c^{\frac{n}{3}}+\frac{m}{6}\frac{\gamma}{RT}c^{\frac{m}{3}}\right) \qquad (13)$$

which allows of the calculation of the lowering of the freezing point or of the raising of the boiling point ($T-T_0$) as a function of the number of molecules present in the solution and of the constants β and Υ.

$$T-T_0=2c\left(1-\frac{n}{6}\frac{\beta}{RT}c^{n/3}+\frac{m}{6}\frac{\gamma}{RT}c^{m/3}\right)\frac{RT_0^2}{r} \qquad (14)$$

As, on the other hand, the lowering or the raising of the transformation point on the basis of the classical theory is given by the expression

$$T-T_0=(1+\alpha)c\frac{RT_0^2}{r} \qquad (15)$$

where α denotes the degree of dissociation, the comparison of equations (14) and (15) yields the relation between the degree of dissociations of the old theory and the constants β and γ of the new theory

$$\alpha = 1 - \frac{n}{3}\frac{\beta}{RT}c^{n/3} + \frac{m\ \gamma}{3RT}c^{m/3} \tag{16}$$

or

$$\frac{\beta}{RT} = \frac{\frac{3}{n}(1-\alpha)}{(c^{1/3})^n} + \frac{m}{n}\frac{\gamma}{RT}(c^{1/3})^{m-n} \tag{17}$$

It is assumed further, in correspondence with experimental data, that $m = 2n$, which gives to equation (17) a very convenient form for experimental verification

$$\frac{\beta}{RT} = \frac{\frac{3}{n}(1-\alpha)}{(c^{1/3})^n} + 2\frac{\gamma}{RT}(c^{1/3})^n \tag{18}$$

$(c^{1/3})^n$ is taken here instead of c^n in order to compare more conveniently the author's constant (18) with Ghosh's constant

$$G = \frac{3(1-\alpha)}{c^{1/3}} \tag{19}$$

Formula (18) was verified on Kohlrausch's conductivity data from which the degree of dissociation was calculated as $\alpha = \lambda/\lambda_0$. On this assumption eg. (16) takes the form

$$\lambda = \lambda_0\left(1 - \frac{n}{3}\frac{\beta}{RT}c^{n/3} + \frac{2n}{3}\frac{\gamma}{RT}c^{2n/3}\right) \tag{20}$$

It is obvious from eq. (20) that the equivalent conductivity λ, and consequently the mobility of ions increases with dilution, and for $c = 0$ reaches its limiting value λ_0. On the other hand, in order to satisfy the condition that, at concentration $c = 1$, λ must be smaller than λ_0, $(\lambda)_{c=1} < \lambda_0$, the following inequality must occur between the constants

$$/\beta/ > /2\gamma/ \tag{21}$$

In the tables below, the constants β/RT (eq. 18) and Ghosh's constants G (eq. 19) are calculated for salt solutions, at the temperature 18°, within a range of concentrations from 0.0001 norm. to 1 norm. In the the headings of columns c denotes the concentration (Kohlrausch's original non-recalculated data), α the degree of dissociation $(\alpha = \frac{\gamma}{\lambda_0})$, G Ghosh's constant (eq. 19), $(c^{1/3})^n$, $G^1 = \frac{\frac{3}{n}(1-\alpha)}{(c^{1/3})^n}$ the first term of eq. (18), and in the last column the constant β/RT. The value of $\frac{2\gamma}{RT}$ is given as the numerical coefficient of $(c^{1/3})^n$ in the equation $\beta/RT = G^1 + 2\frac{\gamma}{RT}(c^{1/3})^n$ above the headings.

TABLE I

Potassium Iodide

$\lambda_0 = 131.1$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.27}$

	c	a	G	$(c^{1/3})^{1.27}$	G^1	β/RT
1	1.0	0.7902	0.629	1.000	0.496	1.10
2	0.5	0.8119	0.711	0.7464	0.595	1.04
3	0.1	0.8694	0.847	0.3772	0.818	1.07
4	0.05	0.8943	0.861	0.2813	0.888	1.06
5	0.02	0.9237	0.843	0.1908	0.944	1.06
6	0.01	0.9414	0.816	0.1423	0.972	1.06
7	0.005	0.9559	0.774	0.1061	0.981	1.05
8	0.002	0.9703	0.707	0.07202	0.974	1.02
9	0.001	0.9781	0.657	0.05370	0.964	1.00
10	0.0005	0.9837	0.616	0.03753	1.026	1.05
11	0.0002	0.9881	0.610	0.02717	1.051	1.05
12	0.0001	0.9902	0.634	0.02026	1.154	1.15

$\beta/RT = 1.06 \pm 5 (\pm 5\%)$

Kohlrausch und von Steinwehr: Sitzungsber. Berl. Akad. 1902, 585.

TABLE II

Potassium Bromide

$\lambda_0 = 132.3$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.30}$

	c	a	G	$(c^{1/3})^{1.30}$	G^1	β/RT
1	0.5	0.7964	0.770	0.7406	0.635	1.08
2	0.2	0.8343	0.850	0.4978	0.768	1.07
3	0.1	0.8634	0.896	0.3684	0.856	1.08
4	0.05	0.8904	0.893	0.2705	0.935	1.10
5	0.02	0.9208	0.875	0.1835	0.996	1.11
6	0.01	0.9401	0.834	1.1359	1.017	1.10
7	0.005	0.9554	0.783	0.1007	1.023	1.08
8	0.002	0.9699	0.717	0.06769	1.027	1.07
9	0.001	0.9781	0.657	0.05012	1.009	1.04
10	0.0005	0.9833	0.631	0.03713	1.038	1.06
11	0.0002	0.9886	0.598	0.02496	1.054	1.07
12	0.0001	0.9913	0.562	0.01847	1.087	1.10

$\beta/RT = 1.08 \pm 2 (\pm 2\%)$

Kohlrausch und von Steinwehr: Sitzungsber. Berl. Akad. 1902, 585.

TABLE III

Potassium Chloride

$\lambda_0 = 130.10$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.35}$

	c	α	G	$(c^{1/3})^{1.35}$	G^1	β/RT
1	1.0	0.7554	0.734	1.0000	0.544	1.44
2	0.5	0.7872	0.804	0.7328	0.646	1.09
3	0.2	0.8299	0.873	0.4846	0.780	1.07
4	0.1	0.8612	0.897	0.3548	0.869	1.08
5	0.05	0.8898	0.897	0.2597	0.943	1.10
6	0.02	0.9223	0.859	0.1681	1.028	1.14
7	0.01	0.9412	0.819	0.1259	1.038	1.11
8	0.005	0.9563	0.766	0.09215	1.054	1.11
9	0.002	0.9709	0.693	0.06102	1.059	1.10
10	0.001	0.9790	0.630	0.04467	1.045	1.07
11	0.0005	0.9847	0.577	0.03273	1.039	1.06
12	0.0002	0.9902	0.503	0.02165	1.006	1.02
13	0.0001	0.9922	0.504	0.01585	1.093	1.10

$\beta/RT = 1.10 \pm 4 (\pm 4\%)$

Kohlrausch und Maltby: Wiss. Abh. Reichsanstalt 3, 154 (1900); Landolt's Tabellen, 1102 (1912).

TABLE IV

Caesium Chloride

$\lambda_0 = 133.6$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.32}$

	c	α	G	$(c^{1/3})^{1.32}$	G^1	β/RT
1	0.1	0.8500	0.970	0.3631	0.939	1.16
2	0.01	0.9371	0.876	0.1318	1.084	1.16
3	0.005	0.9563	0.767	0.09718	1.022	1.08
4	0.002	0.9690	0.738	0.06494	1.085	1.12
5	0.001	0.9779	0.663	0.04786	1.049	1.08
6	0.0005	0.9833	0.631	0.03532	1.074	1.10
7	0.0002	0.9881	0.610	0.02357	1.148	1.16
8	0.0001	0.9904	0.621	0.01738	1.255	1.26

$\beta/RT = 1.12 \pm 4 (\pm 4\%)$

Kohlrausch und von Steinwehr: Sitzungsber. Berl. Akad. 1902, 585.

TABLE V

Potassium Sulphocyanate

$\lambda_0 = 121.3$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.35}$

	c	α	G	$(c^{1/3})^{1.35}$	G^1	β/RT
1	1.0	0.7553	0.734	1.0000	0.544	1.14
2	0.5	0.7891	0.797	0.7328	0.640	1.08
3	0.1	0.8401	1.034	0.3548	1.001	1.21
4	0.05	0.8886	0.907	0.2597	0.953	1.11
5	0.02	0.9200	0.884	0.1720	1.034	1.14
6	0.01	0.9396	0.841	0.1259	1.066	1.14
7	0.005	0.9548	0.793	0.09215	1.087	1.15
8	0.002	0.9701	0.712	0.06102	1.089	1.13
9	0.001	0.9783	0.651	0.04467	1.080	1.11
10	0.0005	0.9842	0.597	0.03273	1.075	1.10
11	0.0002	0.9895	0.539	0.02165	1.129	1.14
12	0.0001	0.9913	0.562	0.01585	1.220	1.23

$\beta/RT = 1.14 \pm 6(\pm 5\%)$

Kohlrausch und von Steinwehr: Sitzungsber. Berl. Akad. **1902**, 585.

TABLE VI

Sodium Chloride

$\lambda_0 = 109.0$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.40}$

	c	α	G	$(c^{1/3})^{1.40}$	G^1	β/RT
1	1.0	0.6822	0.953	1.0000	0.681	1.28
2	0.5	0.7425	0.973	0.7244	0.762	1.20
3	0.2	0.8048	1.001	0.4719	0.887	1.17
4	0.1	0.8443	1.007	0.3414	0.977	1.18
5	0.05	0.8780	0.994	0.2471	1.058	1.21
6	0.02	0.9141	0.950	0.1611	1.143	1.24
7	0.01	0.9353	0.901	0.1166	1.190	1.26
8	0.005	0.9519	0.844	0.08437	1.222	1.27
9	0.002	0.9685	0.750	0.05503	1.227	1.26
10	0.001	0.9772	0.684	0.03981	1.227	1.25
11	0.0005	0.9833	0.631	0.02884	1.241	1.26
12	0.0002	0.9895	0.539	0.01878	1.198	1.21
13	0.0001	0.9917	0.537	0.01359	1.308	1.31

$\beta/RT = 1.24 \pm 6(\pm 5\%)$

Kohlrausch und Maltby: Wiss. Abh. Reichsanstalt **3**, 154 (1900); Landolt's Tabellen, 1102 (1912)

TABLE VII

Potassium Chlorate

$\lambda_0 = 119.7$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.38}$

	c	a	G	$(c^{1/3})^{1.38}$	G^1	β/RT
1	0.5	0.7124	1.086	0.7278	0.859	1.30
2	0.2	0.7818	1.119	0.4769	0.994	1.32
3	0.1	0.8287	1.105	0.3467	1.074	1.32
4	0.05	0.8666	1.094	0.2521	1.150	1.30
5	0.02	0.9090	1.006	0.1612	1.227	1.32
6	0.01	0.9324	0.942	0.1202	1.223	1.29
7	0.005	0.9510	0.860	0.08740	1.219	1.27
8	0.002	0.9679	0.764	0.05735	1.217	1.25
9	0.001	0.9770	0.690	0.04169	1.199	1.22
10	0.0005	0.9831	0.639	0.03034	1.211	1.23
11	0.0002	0.9888	0.575	0.01984	1.228	1.24
12	0.0001	0.9913	0.562	0.01445	1.308	1.32

$\beta/RT = 1.28 \pm 4 (3.5\%)$

Kohlrausch und von Steinwehr: Sitzungsber. Berl. Akad. **1902**, 585.

TABLE VIII

Potassium Nitrate

$\lambda_0 = 126.4$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.45}$

	c	a	G	$(c^{1/3})^{1.45}$	G^1	β/RT
1	1.0	0.6365	1.090	1.0000	0.752	1.35
2	0.5	0.7060	1.111	0.7161	0.849	1.28
3	0.2	0.7811	1.123	0.4593	0.980	1.26
4	0.1	0.8288	1.107	0.3286	1.078	1.27
5	0.05	0.8692	1.065	0.2351	1.152	1.29
6	0.02	0.9114	0.979	0.1509	1.214	1.32
7	0.01	0.9353	0.901	0.1080	1.240	1.31
8	0.005	0.9528	0.828	0.07725	1.264	1.31
9	0.002	0.9699	0.717	0.04962	1.255	1.29
10	0.001	0.9779	0.663	0.03548	1.288	1.31
11	0.0005	0.9840	0.605	0.02541	1.302	1.32
12	0.0002	0.9904	0.493	0.01629	1.230	1.24
13	0.0001	0.9926	0.478	0.01164	1.315	1.32

$\beta/RT = 1.30 \pm 4 (\pm 3\%)$

Kohlrausch und Maltby: Wiss. Abh. Reichsanstalt **3**, 210 (1900).

TABLE IX

Lithium Chloride

$\lambda_0 = 98.89$ $\beta/RT = G^1 + 0.6(c^{2/3})^{1.42}$

	c	α	G	$(c^{1/3})^{1.42}$	G^1	β/RT
1	1.0	0.6406	1.078	1.0000	0.749	1.35
2	0.5	0.7150	1.077	0.7211	0.835	1.27
3	0.2	0.7879	1.088	0.4668	0.960	1.24
4	0.1	0.8333	1.077	0.3362	1.047	1.25
5	0.05	0.8708	1.051	0.2450	1.114	1.26
6	0.02	0.9090	1.006	0.1569	1.254	1.35
7	0.01	0.9317	0.951	0.1131	1.273	1.34
8	0.005	0.9497	0.882	0.08145	1.304	1.35
9	0.002	0.9670	0.786	0.05279	1.320	1.35
10	0.001	0.9759	0.723	0.03802	1.339	1.36
11	0.0005	0.9826	0.658	0.02742	1.310	1.33
12	0.0002	0.9893	0.549	0.01774	1.274	1.29
13	0.0001	0.9924	0.491	0.01278	1.256	1.26

$\beta/RT = 1.32 \pm 5 (\pm 4\%)$

Kohlrausch und Maltby: Wiss. Abh. Reichsanstalt 3, 210 (1900).

TABLE X

Sodium Nitrate

$\lambda_0 = 105.33$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.45}$

	c	α	G	$(c^{1/3})^{1.41}$	G^1	β/RT
1	1.0	0.6253	1.124	1.000	0.775	1.37
2	0.5	0.7031	1.122	0.7161	0.858	1.29
3	0.2	0.7812	1.123	0.4593	0.986	1.26
4	0.1	0.8283	1.110	0.3286	1.081	1.28
5	0.05	0.8680	1.075	0.2351	1.162	1.30
6	0.02	0.9084	1.016	0.1509	1.260	1.35
7	0.01	0.9322	0.944	0.1080	1.299	1.38
8	0.005	0.9499	0.879	0.07725	1.342	1.39
9	0.002	0.9672	0.781	0.04962	1.368	1.40
10	0.001	0.9763	0.711	0.03548	1.382	1.40
11	0.0005	0.9828	0.650	0.02541	1.401	1.42
12	0.0002	0.9893	0.549	0.01630	1.359	1.37
13	0.0001	0.9926	0.478	0.01166	1.313	1.32

$\beta/RT = 1.35 \pm 7 (\pm 5\%)$

Kohlrausch und Maltby: Wiss. Abh. Reichsanstalt 3, 154 (1900); Landolt's Tabellen, 1102 (1912).

TABLE XI

Lithium Nitrate

$\lambda_0 = 95.18$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.43}$

	c	α	G	$(c^{1/3})^{1.43}$	G^1	β/RT
1	1.0	0.6348	1.085	1.0000	0.759	1.36
2	0.5	0.7144	1.079	0.7194	0.833	1.27
3	0.2	0.7881	1.087	0.4643	0.958	1.24
4	0.1	0.8320	1.086	0.3336	1.056	1.26
5	0.05	0.8690	1.067	0.2398	1.147	1.29
6	0.02	0.9078	1.019	0.1549	1.248	1.34
7	0.01	0.9309	0.962	0.1114	1.302	1.37
8	0.005	0.9488	0.898	0.08002	1.343	1.39
9	0.002	0.9661	0.806	0.05170	1.375	1.41
10	0.001	0.9754	0.738	0.03715	1.390	1.41
11	0.0005	0.9824	0.665	0.02673	1.381	1.40
12	0.0002	0.9891	0.559	0.01725	1.325	1.34
13	0.0001	0.9924	0.491	0.01240	1.286	1.29

$\beta/RT = 1.34 \pm 7 (\pm 5\%)$

Kohlrausch und Maltby: Wiss Abh. Reichsanstalt 3, 154 (1900).

TABLE XII

Silver Nitrate

$\lambda_0 = 115.8$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.47}$

	c	α	G	$(c^{1/3})^{1.47}$	G^1	β/RT
1	1.0	0.5837	1.249	1.0000	0.850	1.45
2	0.5	0.6692	1.250	0.7129	0.947	1.38
3	0.1	0.8145	1.199	0.3236	1.170	1.36
4	0.05	0.8592	1.147	0.2304	1.248	1.39
5	0.01	0.9309	0.962	0.1047	1.347	1.41
6	0.005	0.9506	0.867	0.07456	1.352	1.40
7	0.002	0.9683	0.755	0.04760	1.359	1.39
8	0.001	0.9763	0.711	0.03388	1.446	1.46
9	0.0005	0.9833	0.631	0.02415	1.411	1.42
10	0.0002	0.9893	0.549	0.01540	1.386	1.40
11	0.0001	0.9931	0.446	0.01096	1.284	1.29

$\beta/RT = 1.40 \pm 5 (\pm 3.5\%)$

Kohlrausch und von Steinwehr: Sitzungsber. Berl. Akad. 1902, 585.

TABLE XIII

Thallium Nitrate

$\lambda_0 = 127.75$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.44}$

	c	a	G	$(c^{1/3})^{1.44}$	G^1	β/RT
1	0.1	0.7920	1.345	0.3311	1.308	1.51
2	0.05	0.8448	1.264	0.2320	1.361	1.50
3	0.01	0.9268	1.020	0.1096	1.391	1.46
4	0.005	0.9477	0.918	0.07861	1.386	1.43
5	0.002	0.9663	0.802	0.05065	1.386	1.42
6	0.001	0.9757	0.729	0.03631	1.394	1.41
7	0.0005	0.9831	0.639	0.02606	1.357	1.37
8	0.0002	0.9879	0.621	0.01677	1.503	1.51
9	0.0001	0.9913	0.562	0.01202	1.508	1.57

$$\beta/RT = 1.45 \pm 6(\pm 4\%)$$

Kohlrausch und von Steinwehr: Sitzungsber. Berl. Akad. 1902, 585; Landolt's Tabellen, 1102 (1912).

TABLE XIV

Potassium Iodate

$\lambda_0 = 98.50$ $\beta/RT = G^1 + 0.8(c^{1/3})^{1.43}$

	c	a	G	$(c^{1/3})^{1.43}$	G^1	β/RT
1	0.2	0.7546	1.259	0.4643	1.109	1.48
2	0.1	0.8087	1.237	0.3336	1.201	1.47
3	0.05	0.8533	1.195	0.2397	1.283	1.47
4	0.02	0.8997	1.109	0.1549	1.358	1.48
5	0.01	0.9262	1.028	0.1114	1.391	1.48
6	0.005	0.9458	0.951	0.08002	1.421	1.49
7	0.004	0.9510	0.926	0.07194	1.429	1.49
8	0.002	0.9647	0.840	0.05171	1.432	1.47
9	0.001	0.9750	0.750	0.03715	1.412	1.44
10	0.0005	0.9817	0.692	0.02673	1.436	1.46
11	0.0002	0.9881	0.610	0.01725	1.447	1.46
12	0.0001	0.9910	0.582	0.01240	1.489	1.50

$$\beta/RT = 1.47 \pm 3(\pm 2\%)$$

Kohlrausch: Sitzungsber. Berl. Akad. 1900, 1002.

TABLE XV

Sodium Iodate

$\lambda_0 = 77.42$ $\beta/RT = G^1 + 1.0(c^{1/3})^{1.48}$

	c	α	G	$(c^{1/3})^{1.48}$	G^1	β/RT
1	0.2	0.7164	1.455	0.4521	1.272	1.72
2	0.1	0.7809	1.417	0.3210	1.383	1.70
3	0.05	0.8326	1.360	0.2281	1.488	1.72
4	0.02	0.8857	1.264	0.1451	1.597	1.74
5	0.01	0.9154	1.179	0.1031	1.663	1.77
6	0.005	0.9380	1.087	0.07324	1.716	1.79
7	0.004	0.9441	1.056	0.06561	1.723	1.79
8	0.002	0.9598	0.957	0.04662	1.747	1.79
9	0.001	0.9712	0.864	0.03311	1.763	1.80
10	0.0005	0.9797	0.767	0.02355	1.747	1.77
11	0.0002	0.9874	0.646	0.01497	1.706	1.72
12	0.0001	0.9906	0.607	0.01063	1.792	1.80

$\beta/RT = 1.75 \pm 5 (\pm 2.5\%)$

Kohlrausch: Sitzungsber. Berl. Akad. 1900, 1003.

TABLE XVI

Lithium Iodate

$\lambda_0 = 67.34$ $\beta/RT = G^1 + 1.0(c^{1/3})^{1.52}$

	c	α	G	$(c^{1/3})^{1.52}$	G^1	β/RT
1	1.0	0.4426	1.672	1.0000	1.100	2.10
2	0.5	0.5788	1.592	0.7047	1.180	1.89
3	0.2	0.6960	1.560	0.4424	1.356	1.80
4	0.1	0.7647	1.525	0.3114	1.491	1.80
5	0.05	0.8206	1.461	0.2192	1.615	1.83
6	0.02	0.8770	1.359	0.1377	1.762	1.90
7	0.01	0.9095	1.261	0.09696	1.843	1.94
8	0.005	0.9340	1.158	0.06825	1.909	1.98
9	0.002	0.9572	1.019	0.04291	1.968	2.01
10	0.001	0.9692	0.924	0.03020	2.013	2.04
11	0.0005	0.9784	0.816	0.02128	2.004	2.02
12	0.0002	0.9870	0.667	0.01336	1.921	1.93
13	0.0001	0.9908	0.595	0.009404	1.932	1.94

$\beta/RT = 1.94 \pm 12 (\pm 6\%)$

Kohlrausch: Sitzungsber. Berl. Akad. 1900, 1003.

TABLE XVII

Ammonium Chloride

$\lambda_0 = 129.5$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.37}$

	c	a	G	$(c^{1/3})^{1.37}$	G^1	β/RT
1	1.0	0.7491	0.753	1.0000	0.549	1.15
2	0.5	0.7829	0.821	0.7295	0.652	1.09
3	0.3	0.8044	0.876	0.5771	0.742	1.09
4	0.2	0.8224	0.911	0.4795	0.811	1.08
5	0.1	0.8544	0.941	0.3493	0.913	1.12
6	0.05	0.8896	0.899	0.2546	0.950	1.10
7	0.03	0.9097	0.878	0.2017	0.987	1.11
8	0.02	0.9237	0.843	0.1675	0.997	1.10
9	0.01	0.9428	0.797	0.1221	1.027	1.10
10	0.005	0.9586	0.726	0.08896	1.019	1.07
11	0.002	0.9775	0.541	0.05855	0.954	0.99
12	0.001	0.9828	0.516	0.04266	0.883	0.91
13	0.0005	0.9891	0.412	0.03112	0.767	0.79
14	0.0002	0.9941	0.272	0.02046	0.567	0.58

$$\beta/RT = 1.10 \pm 4 (\pm 4\%)$$

Kohlrausch: Landolt's Tabellen, 1103 (1912).

XVIII

Potassium Acetate

$\lambda_0 = 99.60$ $\beta/RT = G^1 + 0.6(c^{1/3})^{1.52}$

	c	a	G	$(c^{1/3})^{1.52}$	G^1	β/RT
1	1.0	0.6365	1.060	1.0000	0.698	1.30
2	0.5	0.7190	1.062	0.7047	0.788	1.21
3	0.3	0.7688	1.036	0.5444	0.840	1.17
4	0.2	0.7950	1.052	0.4424	0.915	1.18
5	0.1	0.8412	1.027	0.3114	1.007	1.19
6	0.05	0.8804	0.974	0.2192	1.077	1.21
7	0.03	0.9026	0.940	0.1692	1.136	1.24
8	0.02	0.9185	0.901	0.1377	1.168	1.25
9	0.01	0.9436	0.786	0.09696	1.148	1.21
10	0.005	0.9605	0.691	0.06670	1.171	1.21
11	0.002	0.9788	0.505	0.04291	0.975	1.00
12	0.001	0.9870	0.390	0.03020	0.850	0.87
13	0.0005	0.9928	0.272	0.02128	0.653	0.66

$$\beta/RT = 1.23 \pm 6 (\pm 5\%)$$

Kohlrausch und Holborn: "Leitvermögen der Elektrolyte", 159 (1898); Landolt's Tabellen, 1103 (1912).

TABLE XIX

Hydrochloric Acid

$\lambda_0 = 379.35$ $\beta/RT = G^1 + 0.4(c^{1/3})^{1.55}$

	c	a	G	$(c^{1/3})^{1.55}$	G^1	β/RT
1*	1.0	0.7932	0.620	1.0000	0.400	0.80
2	0.5	0.8580	0.537	0.6982	0.393	0.67
3	0.2	0.9016	0.505	0.4353	0.438	0.61
4**	0.1	0.9264	0.475	0.3043	0.468	0.59
5	0.05	0.9450	0.448	0.2127	0.501	0.59
6	0.03	0.9557	0.428	0.1634	0.525	0.59
7	0.02	0.9636	0.402	0.1324	0.532	0.59
8	0.01	0.9736	0.368	0.09262	0.552	0.59
9	0.005	0.9822	0.312	0.06474	0.532	0.56
10	0.002	0.9893	0.255	0.04033	0.516	0.53
11	0.0015	0.9902	0.257	0.03395	0.559	0.57
12	0.001	0.9908	0.276	0.02818	0.632	0.64
13	0.00075	0.9917	0.274	0.02429	0.661	0.67
14	0.0005	0.9938	0.240	0.01972	0.608	0.62

$\beta/RT = 0.62 \pm 6 (\pm 10\%)$

*Kohlrausch und Holborn's "Leitvermögen der Elektrolyte" (1898).
**Goodwin and Haskell: Z. physik. Chem. 52, 630 (1905) (Abstract).

TABLE XX

		n	γ/RT	β/RT	Δ %	Class
1	KI	1.27	0.3	1.06	±5%	
2	KBr	1.30	0.3	1.08	±2%	
3	KCl	1.35	0.3	1.10	±4%	1.
4	CsCl	1.32	0.3	1.12	±4%	
5	KSCN	1.35	0.3	1.14	±5%	
6	NaCl	1.40	0.3	1.24	±5%	
7	$KClO_3$	1.38	0.3	1.28	±3.5%	
8	KNO_3	1.45	0.3	1.30	±3%	2.
9	LiCl	1.42	0.3	1.32	±4%	
10	$NaNO_3$	1.45	0.3	1.35	±5%	
11	$LiNO_3$	1.43	0.3	1.34	±5%	
12	$AgNO_3$	1.47	0.3	1.40	±3.5%	
13	$TlNO_3$	1.45	0.3	1.45	±4%	3.
14	KIO_3	1.43	0.4	1.47	±2%	
15	$NaIO_3$	1.48	0.5	1.75	±2.5%	4.
16	$LiIO_3$	1.52	0.5	1.94	±6%	
17	NH_4Cl	1.37	0.3	1.10	±4%	1.
18	KCH_3CO_2	1.52	0.3	1.23	±5%	2.
19	HCl	1.55	0.2	0.62	±10%	

The tabulation of results according to ascending values of β/RT allows of a classification of uni-univalent salts. Four classes can be distinguished with the following characteristics:

Class	β/RT	β/RT	n	n/3	γ/RT
I	1.05—1.15	1.10	1.32	0.44	0.3
II	1.20—1.35	1.30	1.42	0.47	0.3
III	1.40—1.50	1.45	1.45	1.48	0.3—0.4
IV	1.70—2.00	1.85	1.50	0.50	0.5

This classification is very closely related with the ionic mobility. To the first class belong salts whose cations and anions possess simultaneously the highest mobility (on the average 66); to the second class those salts or one both of whose ions do not belong to the quickest type comprised by class I, but neither belongs to the slowest type (average mobility 33); this class is the most common and embraces the majority of salts; the fourth class contains salts one or both of whose ions belong to the slowest type (average mobility 33) but neither to the quickest type. $LiIO_3$ whose cation and anion both possess the lowest mobility 33 is the most striking representative of this class all its constants β/RT, γ/RT and n reaching the highest value.

γ/RT for the first two classes is constant and equal to 0.3. In the last class the value of γ/RT is 0.5. KIO_3 which is composed of a cation of the highest and of an anion of the lowest mobility occupies a transitive position between the fourth and the third class. The inequality (21) $/\beta > /2\gamma/$ obtains in all investigated cases.

The average class value of the exponent n changes symbatically with the class value of β/RT, but within a class the oscillations of n are irregular.

The experimental error $\Delta\%$ oscillates between 2% and 5%. Considering the wide range of concentrations from 0.0001 norm. to 1 norm. and the fact that the theory has been decided for dilute solutions, where different definitions of the concentrations, such as $c = \frac{n_1}{n_0}$, or $c = \frac{n_1}{n_0+n_1+n_2\ldots}$, or $c = \frac{n_1}{\text{Liter}}$, are practically equivalent, the agreement between the theory and experimental data can be considered just as satisfactory as for the dilution law of Ostwald.

Salts undergoing hydrolytic dissociation with liberation of hydrogen (NH_4Cl) or hydroxyl ions (KCH_3CO_2) behave normally down to the concentration 0.005, as can be infered from Tables XVII and XVIII, and possess a constant characteristic of their class; below this concentration and down to 0.0002 norm. the constant falls rapidly. As the degree of hydrolysis increases with dilution and is inversely proportional to the square root of the concentration—the rapid and continuous fall of the constant is due to the increasing influence of the exchange of slow salt ions for very mobile hydrogen or hydroxyl ions.

Hydrochloric acid (Table XIX) behaves differently from salts. In the first place its constant β/RT can be calculated only to 0.5 norm[1], and even in this shorter range the oscillations of its value reach $+10\%$; in the second place, the exponent n, which analogously with results obtained for salts should be less than for KI is, on the contrary, greater than for $LiIO_3$, namely 1.55. Here, obviously, formula (18) which is characteristic of the behaviour of salts cannot be applied with the same degree of accuracy. Thus, the behaviour of strong acids is in some way different from that of salts.

Physical Interpretation

The exponent $n/3$ is very characteristic. In Ghosh's theory its value is $1/3$, and $c^{1/3}$ measures the reciprocal value of the distance between ions. But this statical conception, as was demonstrated by Debye and Hückel[2], is not correct. The treatment of the problem by the methods of statistical mechanics leads to the square root of the concentration instead of the cubic root of Ghosh's theory i.e. to the value of the exponent $1/2$ instead of $1/3$. The value of the exponent, 0.44—0.51, calculated in the present paper yields a strong experimental support to Debye's theory[3].

Debye has given a scientific foundation to Ghosh's hypothesis but did not develop it, therefore, the fact that Debye's formula is applicable only to very dilute solutions can be considered as a definite proof of the incompleteness of Ghosh's conception. Debye and Ghosh consider the ions as points or volumes carrying uniform positive or negative electric charges, and do not take account of the constitution of the ions which follows from Bohr's theory and Kossel's conceptions according to which the ions of the elements adjacent from both sides to the group zero of the periodic system possess the same constitution as the corresponding inert gases of this group. In this way they are constituted of a nucleus carrying a positive charge, and, on the outside, of a very stable kinematic system of eight negative electrons. The difference between positive and negative ions would consist on this assumption in the fact that for positive ions the positive charge of the nucleus is greater than the total negative charge of all the electrons of the ion, while for negative ions it is smaller. At great distances i.e. at great dilutions the integral positive or negative charge of the ions is characteristic of their behaviour, and cations and anions can be considered as positively or negatively charged spheres attracting each other, as is assumed in Debye's theory. But with decreasing distance, i.e., with increasing concentration the repulsion of negatively charged outer rings becomes more and more prominently superposed to the attraction. In the last term of the intrinsic energy of formula (1), $+\gamma(c^{1/3})^n$, account is taken of this repulsion and, as in this way a very satisfactory agreement with experimental data is reached, it must be considered as an important experimental support of treating the ions of electrolytic dissociation as electrostatic spheric doublets with

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[1] At 1.0 norm. the deviation of the constant from the average value attains 30%!

[2] Debye und Hückel: Physik. Z. 24, 185 (1932).

[3] The results of this paper were communicated to the Polish Chemical Congress in Warsaw, April 4th, 1923, before Debye's paper appeared (May 1923).

positive charge in the centre and negative on the surface of the sphere. From this point of view the stability of the exterior electronic ring of the ions is answerable for the fact that oppositely charged ions cannot recombine just in the same way and on the same ground, as for the fact that atoms of inert gases do not combine into molecules with atoms of the same species or into chemical compounds with atoms or molecules of other species. Therefore, this paper must be considered as a strong experimental support of Kossel's hypothesis.

The value of the constant β/RT is characteristic of the electrostatic field created by the ions. In the first class of salts the constant is the lowest and consequently the electric field the weakest. This is in perfect agreement with the fact that K, RC, Cs and Cl, Br, I ions possess the highest mobility, the mobility of ions being on Born's theory[1] the greater the smaller is the electric field created by the ion. On the other hand the ions of class IV, e.g., Li possess the highest value of β/RT and the lowest mobility 33, at the same time their electrostatic field reaches the highest value.

The univalent ions of groups I B and III B of the periodic systema s Ag and Tl behave somewhat differently; inspite of their high mobility 55 and 66 their constant β/RT is greater than for the K and Na ions ($\beta/RT = 1.45$). This points to the difference in the stability of the exterior electronic system in groups zero and eight of the periodic system.

The exceptional constitution of the hydrogen ion which consists of a single positive elementary electric charge is answerable for the fact that acids even the strongest as the hydrochloric acid, are partially dissociated while the electrolytic dissociation of salts is complete. There is no exterior ring of electrons in the hydrogen ion preventing its recombination with anions into a neutral molecule. This is the reason why hydrochloric acid does not obey the same dilution law as the salts (formula 18) and why the majority of organic anions recombines so greatly with the hydrogen ion as to form very weakly dissociated acids.

The same tendency of the hydrogen ion to recombine with correspondingly constituted anions is answerable for the hydrolysis of salts of weak acids. Analogous constitutional reasons, although they are not so obvious, must apply also to the hydrolytic activity of hydroxyl ions.

The physical meaning of formula (20) is obvious. It can be written in the form

$$U = U_0\left(1 - \frac{n}{3}\frac{\beta}{RT}c^{n/3} + \frac{2n}{3}\frac{\gamma}{RT}c^{2n/3}\right) \qquad (22)$$

where U denotes the mobility of the ion.

According to Born[2] the energy of a uniform electrostatic field in which ions move will be used up not only towards the contributions of velocity to ions, but also towards the reconstruction of the electric field whose uniformity is constantly disturbed by the irregular superposition of electrostatic fields due to ionic charges, and towards the setting of the axes of the electrostatic

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[1] Born: Z. Elektrochem. 26, 401 (1920)

[2] Born: Z. Elektrochem. 26, 401 (1920).

doublets of the molecules of the solvent which are continually deviated from the direction of the exterior electrostatic field by collisions with other molecules The work used up for this purpose will be the greater the greater are the electrostatic moments of the molecules of the solvent, but these according to the theory of Sir J. J. Thomson[1] will be increased under the influence of ionic charges which induce upon the molecules of the solvent an additive electrostatic moment. The stronger will be the ionic field, i.e., the greater the concentration, the greater will be also the induced moment, and consequently the greater the energy of the exterior electrostatic field required for the setting of the axes of the doublets. Therefore, the motion of ions in the electric field will be continuously hampered with increasing concentration and the ionic mobility will decrease.

According to this theory the decrease of the equivalent conductivity with concentration is exclusively due to the decrease of the ionic mobility, and thus, the theory of electrolytic dissociation of salts is brought to great simplicity and clearness, and these remains no ambiguity created in the old theory by the necessity of defining and interpreting the degree of dissociation.

Formula (18) is yet capable of further improvement. If we admit with Debye the square root of concentration as a fundamental relation, we can, instead of postulating $m = 2n$, keep n constant and equal to $1/2$, $n = 1/2$, and consider m as variable,

$$\beta/RT = \frac{2(1-)\alpha}{c^{1/2}} + 2m \frac{\gamma}{RT} c^{\frac{2m-1}{2}} \qquad (23)$$

This would follow from the assumption of the function

$$U = N_0U_0 + N_1[u - \beta c^{1/2} + c\gamma^m] \qquad (24)$$

instead of function (1) for the intrinsic energy m would be here slightly different from 1, and its value would be characteristic of the repulsive forces acting between the exterior rings of ions, and consequently of the constitution of the ions.

As the calculations of constants presented in this paper was effected before the appearance of Debye's article I could not make use of his square root relation and therefore could not establish if formula (23) would show as good or a better agreement with experimental data as formula (18). At any rate, before a theory of the phenomenon based on statistical mechanics will be worked out the difference between both formulae must be considered as purely formal. Nevertheless the consideration of formulae (23) and (24) makes it intelligible why the exponents n calculated on the ground of formula (18) are not constant and equal to $1/2$ but vary from 0.44—0.51. Still another reason for the variation of the exponent m can be looked for in the fact that, according to Debye's theory, the constant β is a function of the dielectric constant of the solvent, which increases its value in a yet unknown way with progressing ionic concentration. Such a stipulation is a consequence of electrostatic moments induced upon the electrostatic doublets of the molecules of the solvent by the ionic charges of a strong electrolyte.

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[1] J. J. Thomson: Phil. Mag. 27, 757 (1914).

A STUDY OF THE ELECTROLYTIC DISSOCIATION OF SOME SALTS IN FURFURAL

BY FREDERICK H. GETMAN

According to the familiar Nernst-Thomson[1] hypothesis, the dissociating power of a solvent is largely determined by the magnitude of its dielectric constant. In general, those solvents which possess high dielectric constants cause greater dissociation of a given solute at a given concentration than solvents whose dielectric constants are low. Furfural, $C_5H_4O_2$, has long been known to possess a relatively high dielectric constant, its mean value at 25° being 38. If the more common solvents are arranged in the order of their dielectric constants, furfural is found to stand above such well-known dissociating agents as methyl alcohol, ethyl alcohol, acetonitrile and acetone. Notwithstanding this fact, a search of the literature has failed to reveal sufficient experimental data to warrant any conclusion being drawn as to whether furfural solutions do or do not conform to the Nernst-Thomson generalization.

A few measurements of the conductance of solutions of ferric chloride in furfural were made by Lincoln[2] in the course of a comprehensive study of the conductance of non-aqueous solutions, while Walden[3] has measured the conductance of solutions of his so-called "normal" electrolyte, tetraethylammonium iodide, in furfural at 0° and 25°. Aside from these two series of measurements, there appears to have been little or no attention given to the dissociating power of this solvent.

With a view to contributing something toward this hiatus in the literature of non-aqueous solutions the present investigation was undertaken.

Preparation of Materials. The furfural used in this investigation was obtained from the manufacturer admixed with a relatively small quantity of water. Its purification was effected by a method essentially the same as that described by Mains[4]. A 500 cc. portion was first distilled with the addition of 1 gram of sodium carbonate to neutralize any pyromucic acid which might have been formed as a result of oxidation of the aldehyde. The portion boiling between 159° and 161° was collected and redistilled; the second distillate, consisting of the portion coming over between 160° and 162°, generally possessed some color. After adding granular calcium chloride, the distillate was stored in tightly stoppered flasks in a dark room until required for use. In the final distillation only that portion boiling between 161° and 162° was collected. The mean boiling point, corrected to 760 mm. was 161.7°. The refractive index of the purified solvent was determined and found to be n_D =

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[1] Nernst: Z. phys. Chem., 13, 531 (1894); Thomson: Phil. Mag., (5) 36, 320 (1893).
[2] Lincoln :J. Phys. Chem., 3, 464 (1899).
[3] Wladen: Z. phys. Chem., 54, 150 (1905).
[4] Mains: Chem. Met. Eng. 26, 779 (1922).

1.52717 at 20°, a value in close agreement with that found by Brühl.[1] Because of the rapidity with which the substance polymerizes, a fresh portion was distilled in the preparation of each solution, care being taken to protect the receiver from the light. Notwithstanding the precautions taken in its preparation, the specific conductance of the different portions of furfural was found to vary from 1.38×10^{-6} to 4.77×10^{-6} reciprocal ohms. The mean values of the specific conductance of the furfural used by Lincoln and Walden,[2] respectively, were as follows: 25.6×10^{-6} and 1.45×10^{-6} reciprocal ohms.

The solutes studied in this investigation were the iodides of lithium, ammonium, sodium, potassium and rubidium. The salts were obtained in chemically pure condition and were carefully recrystallized and dried according to the usual prescribed methods. After purification, the salts were preserved in desiccators over sulphuric acid until required for use, when portions were removed and dried to constant weight before dissolving in the solvent and diluting to a definite volume.

Apparatus. The conductance of the solutions was measured in the usual manner by means of the Kohlrausch method. A drum-wound slide-wire bridge with extension coils was used in measuring the conductance of the solutions, an air condenser being employed to balance the effect capacity in the circuit. The resistance boxes were used in series; one a three-dial box ranging in capacity from 1 to 999 ohms and having an accuracy of 0.1 per cent, and the other a two-dial box consisting of Curtis-wound coils ranging in capacity from 1000 to 110000 ohms and having an accuracy of 0.04 per cent. An audio-oscillator giving a frequency of 1000 cycles was used as the source of current together while a specially tuned set of telephone receivers served to determine the position of the tone minimum on the bridge. The conductance cells were of the Arrhenius type with tight-fitting stoppers and sealed-in electrodes. Owing to the ease with which furfural undergoes oxidation, the electrodes were not only not platinized but also were rendered as smooth as possible by polishing with fine emery cloth. The cell constants were determined by means of a 0.01 N potassium chloride solution the specific conductance of which was taken to be 0.001412 reciprocal ohms at 25°. This solution was prepared according to the directions laid down by Kraus and Parker[3]. The values of the cell constants were frequently checked throughout the entire investigation.

All measurements were made at 25°, an electrically controlled thermostat serving to maintain this temperature constant to within 0.01°.

All volumetric apparatus was carefully calibrated for use at prevailing room temperature.

Method and Experimental Results. The mother solutions were prepared by direct weighing, and never more than a single dilution was made from the same mother solution. This procedure was followed in order to minimize

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[1] Brühl: Ann. 235, 1 (1886).

[2] Loc. cit.

[3] Kraus and Parker: J. Am. Chem. Soc., **44**, 2422 (1922).

errors due to polymerization or oxidation of the solvent. In view of the possibility of the solvent undergoing gradual alteration, the conductance of one or more of the solutions was redetermined after an interval of several hours, but in no case was any appreciable change detected. In fact, judging by the gradual change in the color of the pure solvent, on the one hand, and that of the iodide solutions on the other, one is inclined to suspect that the presence of the dissolved substance exerts a stabilizing influence on the solvent. No difficulty was experienced in checking any of the conductance measurements, notwithstanding the comparatively unstable character of the solvent.

The smoothed values of the conductances of the different solutions at even concentrations, as derived from the mean experimental data, are given in the subjoined tables. In these tables C denotes the concentration of the solute in mols per liter of solution, v the corresponding volume, Λ the equivalent conductance, Λ_0 the limiting conductance, and α the conductance ratio, Λ/Λ_0. For comparison, Walden's data for tetraethylammonium iodide[1] are also tabulated..

TABLE I

Conductance of Lithium Iodide in Furfural

C	v	Λ	$\alpha=\Lambda/\Lambda_0$
0.1	10	22.95	0.651
0.05	20	26.25	0.745
0.02	50	29.65	0.841
0.01	100	31.40	0.891
0.005	200	32.68	0.927
0.002	500	33.67	0.955
0.001	1000	34.10	0.968
0.0005	2000	34.40	0.976
0.0	∞	(35.24)	1.000

TABLE II

Conductance of Sodium Iodide in Furfural

C	v	Λ	$\alpha=\Lambda/\Lambda_0$
0.06	16.67	31.15	0.765
0.05	20	31.98	0.786
0.02	50	35.62	0.876
0.01	100	37.72	0.927
0.005	200	39.15	0.962
0.002	500	39.93	0.981
0.001	1000	40.29	0.990
0.0005	2000	40.46	0.904
0.0	∞	(40.70)	1.000

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[1] Walden: Z. phys. Chem. 54, 150 (1905).

Table III

Conductance of Potassium Iodide in Furfural

C	v	Λ	$\alpha=\Lambda/\Lambda_0$
0.1	10	30.50	0.708
0.05	20	33.81	0.784
0.02	50	37.60	0.872
0.01	100	39.99	0.928
0.005	200	41.43	0.961
0.002	500	42.20	0.979
0.001	1000	42.40	0.984
0.0005	2000	42.50	0.986
0.0	∞	(43.10)	1.000

Table IV

Conductance of Rubidium Iodide in Furfural

C	v	Λ	$\alpha=\Lambda/\Lambda_0$
0.07	14.29	33.33	0.740
0.06	16.67	34.10	0.758
0.05	20	34.95	0.776
0.02	50	39.00	0.867
0.01	100	41.10	0.913
0.005	200	42.40	0.942
0.002	500	43.50	0.967
0.001	1000	44.00	0.978
0.0005	2000	44.30	0.985
0.0	∞	(45.00)	1.000

Table V

Conductance of Ammonium Iodide in Furfural

C	v	Λ	$\alpha=\Lambda/\Lambda_0$
0.07	14.29	26.47	0.573
0.06	16.67	27.74	0.602
0.05	20	29.22	0.632
0.02	50	35.45	0.769
0.01	100	38.70	0.840
0.005	200	40.85	0.886
0.002	500	42.67	0.923
0.001	1000	43.65	0.947
0.0005	2000	44.30	0.961
0.0	∞	(46.10)	1.000

Table VI

Conductance of Tetraethylammonium Iodide in Furfural

C	v	Λ	$\alpha=\Lambda/\Lambda_0$
0.005	200	41.40	0.856
0.003	333.3	43.25	0.892
0.002	500	44.23	0.914
0.001	1000	45.47	0.940
0.0005	2000	46.22	0.955
0.0	∞	(48.40)	1.000

The difficulty of securing satisfactory readings at concentrations below 0.0005 N, together with the increase in the magnitude of the errors introduced in corrections for the specific conductance of the solvent, rendered inexpedient any attempts to secure accurate measurements at greater dilutions. The value of the limiting conductance was determined by means of the extrapolation formula recently proposed by Walden[1]. He has furnished a large number of examples of non-aqueous solutions for which the limiting conductance can be satisfactorily calculated by means of the formula—

$$\Lambda_0 = \frac{\Lambda_2(v_2)^{0.45} - \Lambda_1(v_1)^{0.45}}{(v^2)^{0.45} - (v_1)^{0.45}} \qquad (1)$$

in which Λ_1 and Λ_2 are the equivalent conductances at the dilutions v_1 and v_2, respectively. The values of Λ_0 for the solutions of the iodides in furfural, calculated by the above formula, were found to be in almost perfect agreement with the values of Λ_0 determined by the graphic method proposed by Noyes and Falk[2] in which the reciprocal of the equivalent conductance, Λ, is plotted against $(C\Lambda)^m$, m being assigned such a value as shall cause the experimental data to fall on a straight line.

The data of the foregoing tables are also presented in graphic form in Fig. 1 in which the values of the equivalent conductance are plotted against the cube roots of the corresponding concentrations.

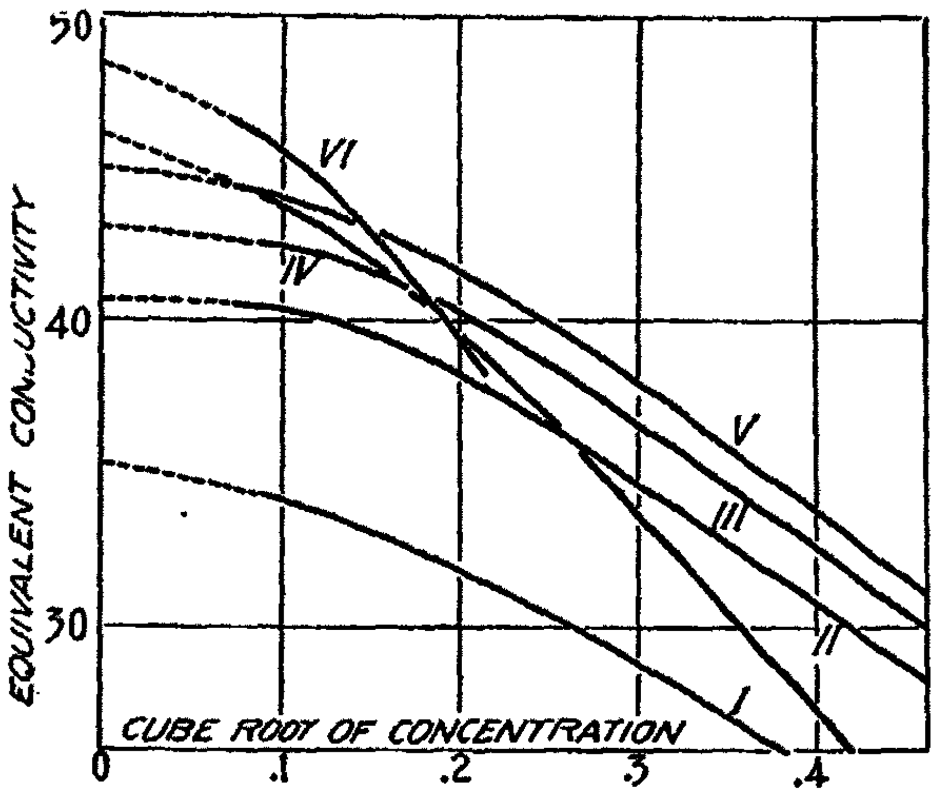

Fig. 1

I. Lithium iodide.
II. Ammonium iodide.
III. Sodium iodide.
IV. Potassium iodide.
V. Rubidium iodide.
VI. Tetraethylammonium iodide

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[1] Walden: Z. anorg. Chem. 115, 57 (1921).
[2] Noyes and Falk: J. Am. Chem. Soc. 34, 454 (1912).

Discussion of Results. It will be observed that the curves shown in Fig. 1 tend to arrange themselves in two distinct groups according to the rate at which the conductance changes with the concentration. The first group comprises the iodides of lithium, sodium, potassium and rubidium, while the second includes the iodides of the ammonium radical. This difference in the slope of the conductance curves of the alkaline iodides, on the one hand, and of the ammonium iodides, on the other, is noteworthy. In aqueous and alcoholic solutions, the form of the conductance curves of ammonium salts, in general, bears a close resemblance to that of the salts of the alkali metals. If tetraethylammonium iodide, Walden's typical binary electrolyte, behaves in furfural in a perfectly normal manner, then it follows that the iodides of the alkali metals are abnormal in their behavior in this solvent. On the other hand, the difference in the form of the two groups of conductance curves may be attributed to the tendency of aldehydes to form complexes with the ammonium radical.

It is also of interest to point out that none of the six salts under consideration conform to an interesting relation recently discovered by Walden[1], involving the dielectric constant and the viscosity of the solvent. Walden has shown that for a large number of dilute solutions, the product of the viscosity, η, and the dielectric constant, D, of the solvent, multiplied by the dilution, $(v)^{0.45}$, and the corresponding value of $\Lambda_o - \Lambda_v = d_v$ is equal to a constant, 51.4; i.e.,

$$K = \eta D(v)^{0.45} d_v = 51.4. \qquad (2)$$

The values of K for dilute solutions of the salts included in this investigation are given in Table VII.

TABLE VII

Values of $K = D(v)^{0.45} d_v$ for Furfural Solutions

$\eta^{25°} = 0.0149$, $D_{25°} = 38$.

Dilution	LiI	NaI	KI	Rbi	NH_4I	$(C_2H_5)_4NI$
500	14.57	7.14	8.35	31.92	31.84	38.70
1000	14.45	5.20	8.87	12.68	31.06	37.15
2000	14.55	4.16	8.66	12.13	31.18	37.76
	(14.52)	(5.50)	(8.63)	(12.91)	(31.36)	(37.87)

Although the values of K for the individual salts are approximately constant they differ widely from each other and from the mean value 51.4, found by Walden for several binary electrolytes in sixteen different solvents. It would be of interest to know why furfural solutions fail to conform to this relationship.

The fact that the values of the conductance of the iodides of lithium, sodium, potassium and rubidium in furfural stand in the inverse order of the molecular weights of the solutes may be regarded as an indication of ionic solvation. The degree of ionic solvation may be calculated, according to Walden[2], from a knowledge of the limiting conductance, Λ_o, of the solute, its

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[1] Walden: Z. anorg. Chem. 115, 73 (1921).

[2] Walden: Z. Elektrochem. 26, 65 (1920).

molecular weight, M, the viscosity of the solvent, η, and the molecular weight, M_o, of the latter. Walden showed that the value of the constant in the equation

$$\Lambda_o\eta_o = K', \qquad (3)$$

is dependent upon the molecular weight of the solute; and that for solutions of different solutes in various solvents, the product of the limiting value of the conductance, the viscosity of the solvent and the square root of the molecular weight of the solute remains constant at 25°; i.e.,

$$\Lambda_o\eta_o\sqrt{M} = 11.15 \qquad (4)$$

When the ions of the solute are solvated, its molecular weight will obviously be increased. Under these conditions, if the solute is not polymerized, the value of the constant in equation (4) will be less than 11.15, and the weight of solvent associated with the ions will be given by the equation

$$W = \left(\frac{11.15}{\Lambda^{\circ}\eta_o}\right)^2 - M \qquad (5)$$

Hence, the number of mols of solvent associated with the ions will be W/M_o. Walden states that the iodide ion is not solvated in ethyl alcohol, methyl alcohol, acetone or nitrobenzene; therefore, it may be assumed that its tendency to undergo solvation in furfural is negligible. On this assumption the degree of solvation of the cations of the six salts included in this investigation has been calculated as shown in the following table.

TABLE VIII

Degree of Solvation of Cations in Furfural

Solute	LiI	NaI	KI	RbI	NH_4I	$(C_2H_5)_4NI$
W/M_o	3.30	3.52	1.44	0.67	1.24	0

On the assumption that the chloride ion is not hydrated, the calculated values of the degree of hydration of some of the above ions in water is as follows:—Li, 4.7, Na 2.0, and K 1.3.[1] These figures, it will be seen, are of the same order of magnitude as those calculated for the same ions in furfural as a solvent.

The variation of the conductance of the iodide solutions in furfural with concentration is found to be accurately expressed by the equation derived by Storch[2], who showed that the functional relation between conductance and concentration can be expressed by means of the equation

$$\Lambda_o - \Lambda = K\Lambda^n C^{n-1} \qquad (6)$$

The exponent *n* is varied as required by the experimental data. In the case of aqueous solutions, this equation has been found to apply over a comparatively wide range of concentrations. The Storch equation has the advantage that it

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[1] Washburn and Millard: J. Am. Chem. Soc., 37, 694 (1915).

[2] Storch: Z. phys. Chem., 19, 13 (1896).

expresses the concentrations of both the dissociated and undissociated portions of the solute as a function of each other. This becomes apparent when equation (6) is written in the form

$$C(\Lambda_0 - \Lambda) = K(\Lambda C)^n, \qquad (7)$$

which is obviously equivalent to

$$C(1 - \alpha) = \text{Constant} \times (C\alpha)^n, \qquad (8)$$

where α is the conductance ratio, Λ/Λ_0. On plotting the values of $1/\Lambda$ against those of $(C\Lambda)^m$, where $m = n - 1$, and assigning successive numerical values to the exponent until the points fall as nearly as possible on a straight line, the three arbitrary constants, n, K and Λ_0 can be evaluated. The subjoined table gives the values of n thus obtained for the six different salts in furfural solution.

TABLE IX

Values of n in the Function $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$ at 25°.

Solute	LiI	NaI	KI	RbI	NH_4I	$(C_2H_5)_4NI$
n	1.75	1.80	1.85	1.75	1.90	1.70

The mean value of n for aqueous solutions of these same salts is approximately 1.50. As has already been mentioned, the values of Λ_0 as determined by the graphic method described above are in remarkably close agreement with those obtained by means of Walden's extrapolation formula.

In conclusion attention should be directed to the fact that the values of the conductance ratio, Λ/Λ_0, in Tables I-VI, are relatively high. If this ratio affords a true measure of the degree of electrolytic dissociation of these salts when dissolved in furfural, it follows that the latter is to be ranked among the best known dissociating agents, and offers additional confirmation of the validity of the Nernst -Thomson relation.

Summary. (1) The conductance of solutions of six different binary electrolytes (LiI, NaI, KI, RbI, NH_4I and $(C_2H_5)_4NI$) in furfural has been studied. The value of the limiting conductance, Λ_0, has been determined by extrapolation and the values of the conductance ratio, Λ/Λ_0, at concentrations ranging from 0.1 N to 0.0005 N have been calculated. These ratios are found to be relatively high, from which it follows that furfural is to be regarded as a solvent possessing high dissociating power, provided that the conductance ratio affords a true measure of the degree of electrolytic dissociation.

(2) When the conductances are plotted against the cube roots of the concentrations, it is found that the values of the conductance of solutions of ammonium iodide and tetraethylammonium iodide increase more rapidly with dilution than do the corresponding values of the conductance of solutions of the iodides of lithium, sodium, potassium and rubidium. This difference between the behavior of the ammonium salts on the one hand, and that of the alkali iodides on the other, may be due to the tendency of the ammonium radical to react with the aldehydic solvent, or it may be ascribed to some abnormality in the dissociation of the alkali iodides in furfural.

(3) None of the furfural solutions studied in this investigation conform to the relation deduced by Walden involving the viscosity and the dielectric constant of the solvent, viz.,

$$K = \eta_o D(v)^{0.45} d_V = 51.4$$

(4) The degree of solvation of the cations of the different salts has been calculated and found to be approximately of the same order of magnitude as in aqueous solutions.

(5) The Storch equation has been shown to express the functional relation between conductance and concentration of the solutions of the different salts with considerable accuracy, the value of the exponent, n, in the equation

$$C(\Lambda - \Lambda_o) = K(C\Lambda^n)$$

being greater than in the case of the corresponding aqueous solutions.

Hillside Laboratory
Stamford, Conn.
June 20, 1923.

THE INFLUENCE OF CERTAIN CHEMICALS ON THE RATE OF REPRODUCTION OF YEAST IN WORT

BY NORMAN A. CLARK

In a paper[1] "The Rate of Formation and Yield of Yeast in Wort" I have shewn that if wort be seeded with "normal" actively-budding yeast cells and the culture be properly shaken and aerated, at 25°C the rate of reproduction follows the "logarithmic law"[2] $\log C/C_0 = k.t$ from the moment of seeding until the crop reaches 100 million cells per cubic centimeter when the alcohol formed during fermentation begins to have an effect; diluting the wort with a solution of sugar and salts, or adding small amounts of alcohol have no effect on the (initial) rate of reproduction. The experiments described in the present paper were carried out in the winter of 1920-21 together with those just referred to; all measurements were made at 25°C; yeast, wort and apparatus were the same as in my experiments with alcohol, and the technique was that described in my previous paper except that the counting was done under the microscope without the use of photography.

Phenol

In Table I (and in the other tables) the numbers under *t* give the time in hours between seeding and counting; those under *log C* give the common

TABLE I (Phenol)

0.00%		0.02%		0.04%		0.06%	
t	Log C	t	Log C	t	Log C	t	Log C
0.0	1.46	0.0	1.46	0.0	1.46	0.0	1.46
6.0	2.42	1.3	1.57	1.6	1.62	2.0	1.69
24.0	3.11	2.8	1.75	3.0	1.84	3.2	1.80
		6.3	2.33	6.7	2.34	6.8	2.37
		24.0	3.10	24.0	3.02		
0.08%		0.10%		0.12%		0.14%	
0.0	1.46	0.0	1.46	0.0	1.46	0.0	1.46
1.3	1.52	1.5	1.58	1.7	1.52	1.8	1.55
2.5	1.73	2.6	1.68	2.8	1.69	3.0	1.58
5.0	2.10	5.2	1.98	5.4	1.96	5.6	1.92
24.0	3.00	6.6	2.14	6.8	2.14	7.0	2.02
		24.0	2.93	24.0	2.82	24.0	2.66
0.16%		0.18%		0.20%		0.22%	
0.0	1.45	0.0	1.45	0.0	1.45	0.0	1.45
1.7	1.47	2.1	1.45	2.2	1.45	26.0	1.45
2.7	1.50	2.8	1.48	3.0	1.45		
5.0	1.55	5.2	1.49	6.5	1.47		
7.1	1.74	7.3	1.54	8.2	1.48		
9.0	1.81	8.7	1.60	24.2	1.54		
10.8	1.88	11.1	1.64				
25.0	2.33	24.4	1.78				

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[1] J. Phys. Chem. 26, 42 (1922)

[2] $k=0.160$; C=count at the time t; C_0=count at $t=0$; t=interval in hours between seeding and counting. The "count" multiplied by 250000 gives the number of yeast cells in one cubic centimeter of the culture medium.

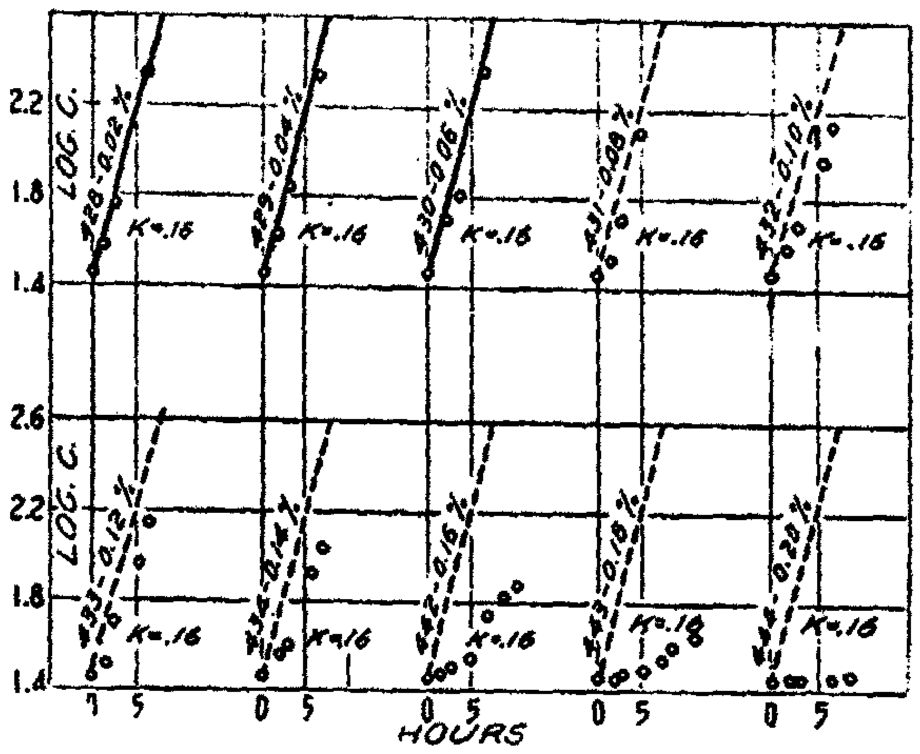

Fig. 1

logarithm of the "count"; the number of cells per cc of culture medium is 250000 C. The number of grams of phenol contained in 100cc of the culture medium is given at the head of the columns as "% phenol". In Fig. 1, log C is plotted against *t*; the straight line gives the values of log C that would be obtained in absence of phenol (k = 0.160).

Inspection shews that in solutions containing 0.06% phenol the rate of reproduction is just distinguishably less than in pure wort; with 0.10% the retardation is unmistakable, and increases with further increase in the concentration of the phenol. In wort containing 0.22% phenol reproduction ceases entirely, no increase in the number of cells could be observed after seven days at 25°C; this might be taken as evidence that all the cells were promptly killed by the poison, but after 48 hours only 4% of them were stained by methylene blue[1]. To settle the matter, cultures were made after 48 hours and after 72 hours in the 0.22% phenol; the cells were removed by filtration, washed with sterile water, placed in a shaker tube with fresh wort at 25°C, and counts made as usual (see Table II). After a resting period of about three hours, reproduction set in at the normal rate (k = 0.16); phenol of this concentration (0.22%) evidently prevents reproduction without destroying life; no evidence of spore formation was observed; data in Fig. 2.

Table II (Phenol)

After 48 hours		After 72 hours	
t	Log C	t	Log C
0.0	0.95	0.0	0.87
2.5	0.94	1.5	0.87
3.3	1.03	2.5	0.87
5.2	1.38	3.3	0.96
6.5	1.63	7.0	1.33
		8.4	1.64

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[1] Fraser: J. Phys. Chem. 25, 20 (1921)

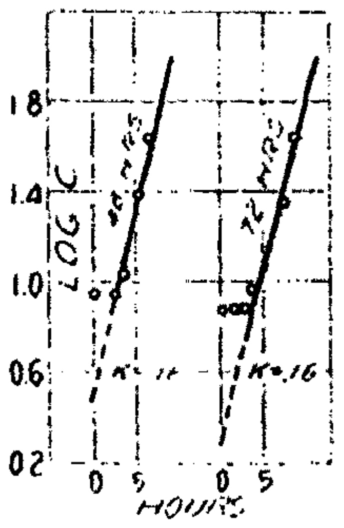

Fig. 2

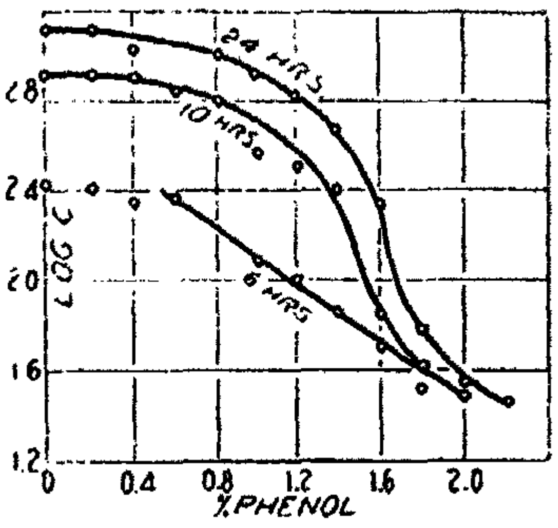

Fig. 3

Values of log C for $t=6$ and various concentrations of phenol from 0.06% to 0.20% phenol (obtained by interpolation from Table I) are shewn in Fig. 3; the points fall on a straight line, and (for $t=6$) $\log C/C_0 = 6(0.20 - \%)$; for lower concentrations of phenol the count is much less than corresponds to this equation, due no doubt to the influence of the alcohol formed during the fermentation; the same explanation may be put forward to account for the form of the log C curves for $t = 10$ and $t = 24$ of the same figure.

Methyl Green

The effect of methyl-green on yeast has been studied by Fraser[1]; it has since been found to act very much like ammonium fluoride[2]. Yeast can become "acclimatized" to it i.e. by gradually increasing the concentration of the methyl-green yeast can be bred to reproduce in solutions in which "normal" yeast will not increase. Like ammonium fluoride, too, methyl-green causes the yeast cells to grow in clusters; the cell buds in the usual way, but the daughter-cell develops slowly, and before it has attained full size the mother-cell buds again in a different place; seven or eight daughter-cells each rather more than half the normal size have been seen attached to the same mother-cell; frequently the daughter-cells bud without separating from the parent. When these bunches are large, accurate counting is an impossibility.

As shewn in Table III and Fig. 4 the initial rate of reproduction is not greatly affected until the methyl-green reaches a concentration of 0.01%; with five times that concentration no reproduction was observed in 10 hours, but after six days the count was four times as great as at the moment of seeding. At $t=6$, $\log C/C_0 = 33(0.03 - \%)$ for values of % from 0.0 to 0.027.

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[1] J. Phys. Chem. 25, 20 (1921)

[2] Fulmer: J. Phys. Chem. 25, 10 (1921)

TABLE III (Methyl Green)

0.0015%		0.003%		0.005%		0.007%		0.010%	
t	Log C	t	Log C	t	Log C	t	Log C	t	Log C
0.0	1.43	0.0	1.43	0.0	1.43	0.0	1.43	0.0	1.43
1.75	1.68	2.0	1.69	2.25	1.74	2.6	1.78	2.0	1.67
6.2	2.35	5.5	2.17	5.2	2.11	4.8	2.09	4.75	2.0

0.014%		0.016%		0.02%		0.024%		0.027%	
0.0	1.43	0.0	1.43	0.0	1.43	0.0	1.43	0.0	1.43
2.2	1.58	2.3	1.51	1.8	1.52	2.0	1.45	2.3	1.47
5.2	1.86	5.5	1.82	3.3	1.52	5.2	1.54	5.3	1.50
7.3	2.06	7.6	1.97	5.0	1.59	7.3	1.62	7.7	1.57
				7.1	1.79	18.8	2.02	18.5	1.96
				19.0	2.16	24.0	2.21	24.0	2.08
				24.0	2.51				

0.03%		0.035%		0.04%		0.05%	
0.0	1.43	0.0	1.43	0.0	1.43	0.0	1.43
3.1	1.48	3.3	1.46	8.1	1.50	6.0	1.42
5.5	1.49	5.7	1.50	17.5	1.60	8.3	1.40
18.3	1.96	7.9	1.49	24.0	1.80	17.3	1.54
24.0	2.12	17.9	1.78			21.3	1.49
		24 0	1.97			24.0	1.54
						140.0	±2.00

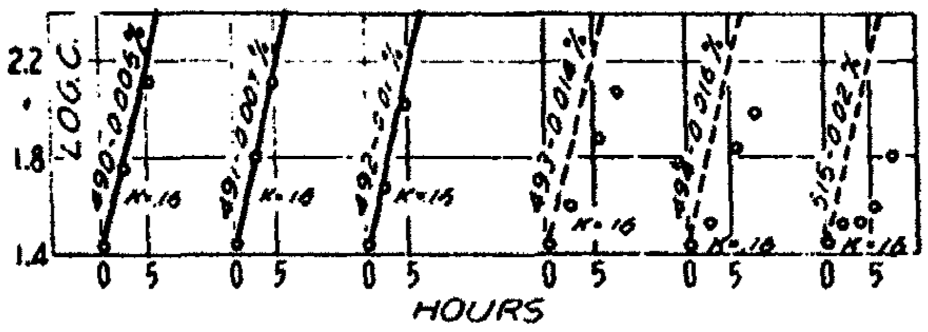

FIG. 4

Acetone

One gram of acetone in 100cc of its solution in wort (1.0 % acetone) barely slowed the rate of reproduction; (see Table IV and Fig. 5); after 24 hours in 5.5% acetone reproduction had hardly commenced and methylene-blue stained 34% of the cells, after 48 hours there were about four times as many cells present as originally added. In these strong solutions the cells were a good deal bunched, but in dilute acetone solutions the bunching is noticeably less than in pure wort[1]. Taking advantage of this peculiarity, the measurements were repeated (Table V) with a low seeding, about one-seventieth of that employed in the experiments of Table IV; the results confirm those already obtained.

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[1] A small addition of phenol to wort also reduces the bunching.

TABLE IV (Acetone)

1%		2%		3%	
t	Log C	t	Log C	t	Log C
0.0	1.37	0.0	1.37	0.0	1.37
2.2	1.67	2.4	1.55	2.7	1.47
4.8	2.06	5.0	1.97	5.3	1.81
7.3	2.35	7.5	2.28	7.7	2.09
24.0	3.09	24.0	3.12	24.0	2.98

4%		5%		5.54%	
0.0	1.27	0.0	1.37	0.0	1.37
2.5	1.42	2.4	1.38	2.2	1.35
4.8	1.46	4.6	1.36	5.0	1.37
6.1	1.56	6.2	1.38	9.7	1.37
10.1	1.90	10.0	1.43	13.2	1.37
24.0	2.75	13.4	1.52	23.0	1.46
		23.2	1.86	48.0	1.98

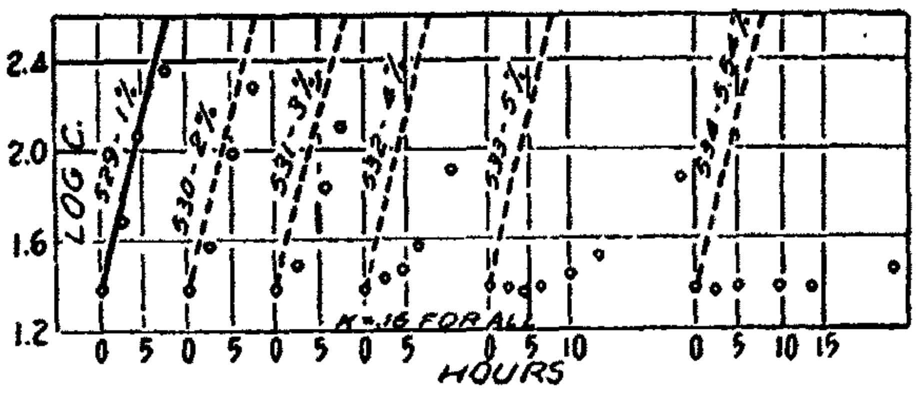

FIG. 5

TABLE V (Acetone)

0.0%		1%		2%	
t	Log C	t	Log C	t	Log C
0.0	−0.46	0.0	−0.46	0.0	−0.46
9.5	+1.09	9.8	+1.05	10.0	+0.74
12.8	1.68	11.8	1.36	12.2	1.07
14.7	1.98	15.1	1.88	15.4	1.51
24.0	3.10	24.0	3.04	17.5	1.82
				24.0	2.59

3%		4%		5%	
0.0	−0.46	0.0	−0.46	0.0	−0.46
15.0	+0.82	17.2	+0.34	34.2	+0.11
17.4	1.10	20.6	0.52		
20.8	1.59	24.0	0.66		
24.0	1.95				

The relation between the crop at 6, 10, or 24 hours and the percentage of acetone in the wort is represented fairly well by the equation log $C/C_0 = 0.039\ t\ (5.0-\%)$, which holds both for light and for heavy seeding for concentrations down to 1.0% (below which the rate is not affected) or until log $C = 2.6$ (interference by alcohol) whichever occurs first.

TABLE VI (Acetone)

t	0.0	10.8	15.8	24.3
Log C	1.48	2.01	2.31	2.62

In an experiment in which a 5% solution of acetone in wort was rocked at 25° C for 24 hours before seeding with yeast, reproduction began at once without the delay observed when the acetone was added immediately before seeding, and proceeded regularly (k=0.05) for 24 hours (see Table VI); this observation seems to indicate some slow reaction between the acetone and wort or one of its constituents. Another experiment affords direct evidence of adaptation of the yeast to acetone:—Ten hours after seeding a 5% solution of acetone in wort, when reproduction was just beginning, the yeast cells were filtered off and placed in a freshly prepared 5% solution (Table VII A). while the filtrate was seeded with normal yeast (Table VII B); the treated yeast (A) began reproduction at once (k=0.03), while the normal yeast delayed for three hours, and then multiplied with k=0.08

TABLE VII (Acetone)

VIIA

t	0.0	3.8	6.6	7.6	12.1
Log C	1.87	1.93	2.09	2.10	2.21

VIIB

t	0.0	3.7	6.6	12.0
Log C	1.65	1.72	1.94	2.38

Sodium Bicarbonate

Addition of sodium bicarbonate to wort produces a heavy precipitate; this was removed by a centrifuge and the clear liquid inoculated etc as usual. Besides the results recorded in Table VIII and Fig. 6, measurements were made with solutions prepared from 0.0, 0.011, 0.022, 0.033, 0.045, 0.056, 0.067 and 0.078 formula weights $NaHCO_3$ per litre of wort; in all these solutions reproduction followed the logarithmic law with k=0.16, so there is no need to record the figures. The results of Table VIII shew that up to 0.116 $NaHCO_3$ per litre reproduction is the same as in pure wort (k=0.16). but that at 0.175 there was a pause, or period of very slow reproduction followed by reproduction with k=0.12; further increase in the amount of bicarbonate increased the duration of the pause and decreased the subsequent rate of reproduction, until with 0.58 $NaHCO_3$ per litre no reproduction took place even after 108 hours. After 60 hours in this concentrated solution, 98 to 99% of the cells were stained by methylene-blue, but even after 84 hours some were still alive, for at that time 0.5 cc of the suspension was mixed with pure wort, and in two days active fermentation had set in, and the culture contained a large number of cells.

TABLE VIII (Sodium Bicarbonate)

0.080FW		0.116FW		0.175FW		0.203FW	
t	Log C	t	Log C	t	Log C	t	Log C
0.0	1.15	0.0	1.15	0.0	1.15	0.0	1.06
0.75	1.23	1.0	1.27	1.0	1.18	1.0	1.03
1.25	1.26	2.2	1.42	1.75	1.19	3.2	1.17
2.0	1.42	5.0	1.90	2.5	1.26	4.3	1.23
4.7	1.99	7.7	2.32	4.3	1.48	5.7	1.32
7.5	2.38			5.5	1.55	7.0	1.56
				6.8	1.75	9.2	1.65
				7.8	1.88	11.1	1.94
				10.2	2.21		
				11.7	2.36		

0.232FW		0.291FW		0.580FW	
0.0	1.15	0.0	1.15	0.0	1.06
1.3	1.19	1.5	1.18	1.4	1.05
2.9	1.22	3.2	1.20	4.5	1.08
4.7	1.42	4.8	1.22	6.1	1.06
5.9	1.49	6.2	1.34	7.7	1.03
7.2	1.72	7.4	1.45	10.7	1.08
8.2	1.76	8.5	1.46	13.5	1.08
10.6	1.97	10.7	1.66	23.5	1.05
12.1	2.14			29.5	1.04
				36.3	1.02
				47.0	1.05
				55.0	1.05
				108.0	±1.05

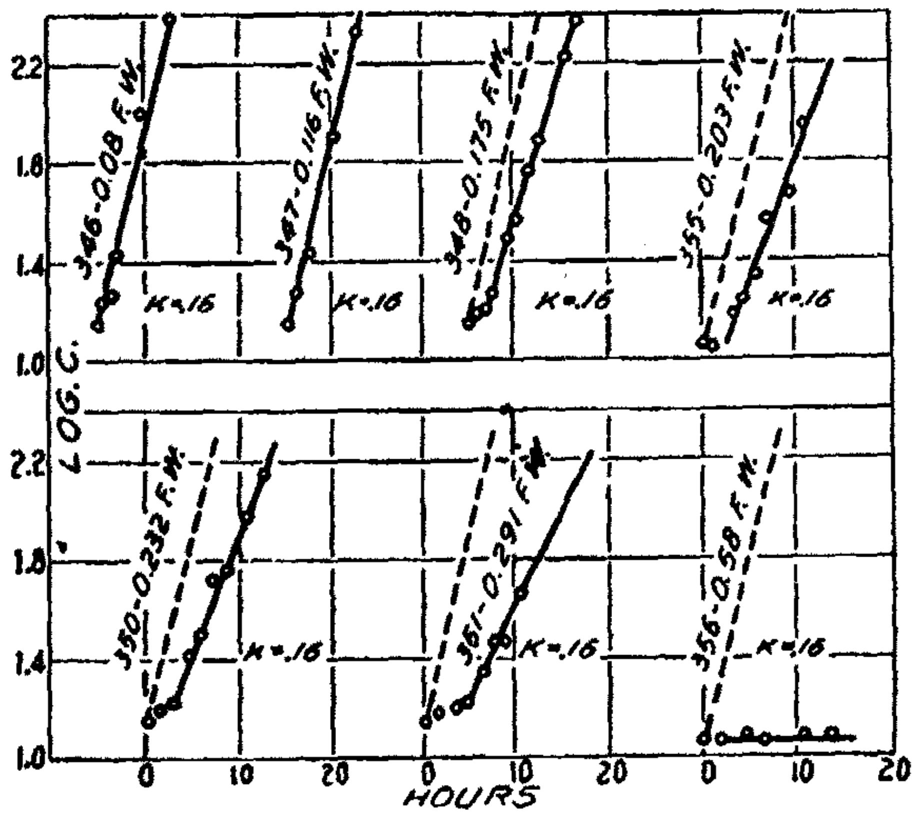

FIG 6

Mr. P. J. Moloney was kind enough to help me determine the P_H values given in Table IX using his new form of hydrogen electrode[1]; taken in

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[1] J. Phys. Chem. 25 758 (1921).

conjunction with the results of Table VIII, they shew that reproduction occurs at the normal rate only when the solution is on the acid side of the neutral point.

TABLE IX (Sodium Bicarbonate)

$NaHCO_3$ per L.	0.00	0.116	0.175	0.291
P_H	4.11	6.80	7.08	7.31

In a few experiments sodium bicarbonate was added to wort-agar (2% agar), and after seeding with yeast plates were poured; the effect of the alkali was much more pronounced than in the liquid medium. With 0.328, 0.208 or even 0.116 $NaHCO_3$ per litre of wort, only one or two colonies appeared on each plate, while the check plates with no alkali shewed fifty.

Hydrochloric Acid

Table X and Fig. 7 give the rate measurements, and Table XI the P_H measurements. Up to 0.055 formula-weights HCl per litre (P_H=3.06) the rate of reproduction is normal (k=0.16), but with 0.06 HCl (P_H=2.98) there is perceptible retardation; with 0.105 HCl the count increases only 25% in 12 hours, and with 0.115 HCl the increase in 36 hours was hardly perceptible. The "initial lag" (period of rest or very slow reproduction) was less marked than with bicarbonate; with 0.08 HCl per litre, where *k* lies between 0.12 and 0.13, five determinations made at intervals during the first 90 minutes shewed no sign of variation in the rate of reproduction; with 0.09 HCl there was some indication of an initial pause, and this was quite pronounced with 0.10 HCl.

TABLE X (Hydrochloric Acid)

0.00FW		0.011FW		0.024FW		0.055FW		0.060FW	
t	Log C	t	Log C	t	Log C	t	Log C	t	Log C
0.00	1.49	0.00	1.49	0.00	1.49	0.00	1.49	0.00	1.32
4.7	2.34	1.0	1.54	1.2	1.51	0.8	1.59	1.0	1.32
		5.0	2.32	2.0	1.72	1.8	1.63	1.9	1.42
				3.2	1.94	2.9	1.80	2.7	1.67
				5.2	2.27	4.8	2.14	5.6	2.02
						5.8	2.38	7.2	2.24

0.070FW		0.080FW		0.090FW		0.095FW		0.105FW	
0.0	1.32	0.0	1.32	0.0	1.32	0.0	1.54	0.0	1.54
1.25	1.32	1.3	1.33	2.5	1.37	1.0	1.58	12.6	1.65
2.2	1.52	2.3	1.42	3.3	1.44	2.6	1.60		
2.7	1.70	3.1	1.62	4.5	1.66		*		
5.3	2.0	4.9	1.91	6.5	1.79				
7.5	2.29	7.7	2.19	8.0	1.98				

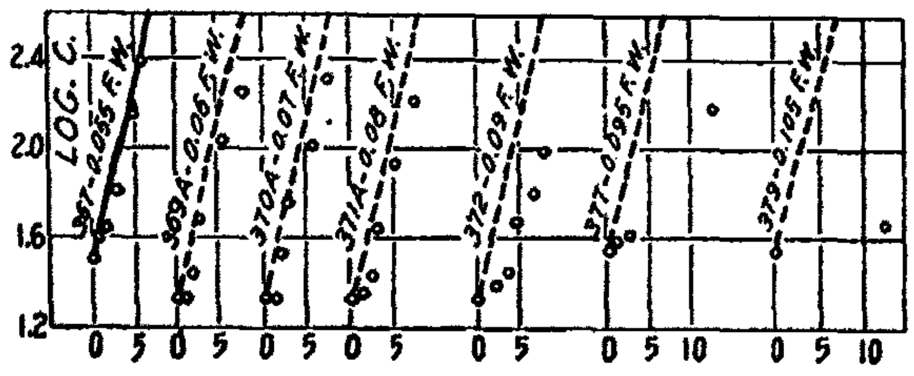

FIG. 7

TABLE XI (Hydrochloric Acid)

HCl per L	0.00	0.011	0.055	0.090	0.110
P_H	4.03	3.84	3.06	2.47	2.20

On two per cent agar-wort plates addition of 0.08 HCl per litre caused no decrease in the number of colonies, but their growth was somewhat slow; with 0.10 HCl duplicates were difficult to obtain, and with 0.115 HCl no colonies appeared. After five hours in wort with 0.10 HCl, six per cent of the cells stained with methylene-blue.

Acetic Acid

The results recorded in Table XII and Fig. 8 shew that equivalent quantities of acetic and hydrochloric acids have much the same effect on the reproduction of yeast; they have very different effects on the acidity of the solution (Table XIII, P_H). Reproduction is retarded between 0.06 and 0.07 $C_2H_4O_2$ per litre as compared with 0.06 HCl; initial lag is noticeable in solutions containing 0.09 formula-weights per litre of either acid; in solutions containing 0.13 $C_2H_4O_2$ per litre there is no appreciable reproduction in the first ten hours, the same was true with 0.105 HCl. On wort-agar plates, 0.06 $C_2H_4O_2$ per litre gave the same number of colonies as the check plates and they developed as quickly; with 0.09 $C_2H_4O_2$ the colonies appeared later, and in most cases were slightly less numerous than the checks.

TABLE XII (Acetic Acid)

0.04FW		0.06FW		0.07FW		0.08FW		0.09FW	
t	Log C	t	Log C	t	Log C	t	Log C	t	Log C
0.0	1.42	0.0	1.38	0.0	1.38	0.0	1.44	0.0	1.46
1.0	1.56	1.2	1.62	0.5	1.40	0.6	1.47	1.1	1.53
2.5	1.85	2.5	1.69	1.4	1.55	1.2	1.49	2.8	1.66
		6.0	2.20	2.8	1.72	1.7	1.56	5.3	1.89
				5.5	2.05	2.7	1.67	6.9	2.07
						3.2	1.72		
						5.2	2.04		
						6.7	2.26		

0.10FW		0.11FW		0.12FW		0.13FW	
0.0	1.48	0.0	1.54	0.0	1.54	0.0	1.54
1.3	1.52	1.5	1.59	1.7	1.55	0.75	1.54
3.0	1.57	3.2	1.56	3.4	1.49	2.0	1.53
5.7	1.76	5.7	1.67	6.4	1.59	8.0	1.53
7.2	1.95	7.3	1.72	7.7	1.64		
8.5	2.14	10.2	2.08	10.5	1.73		

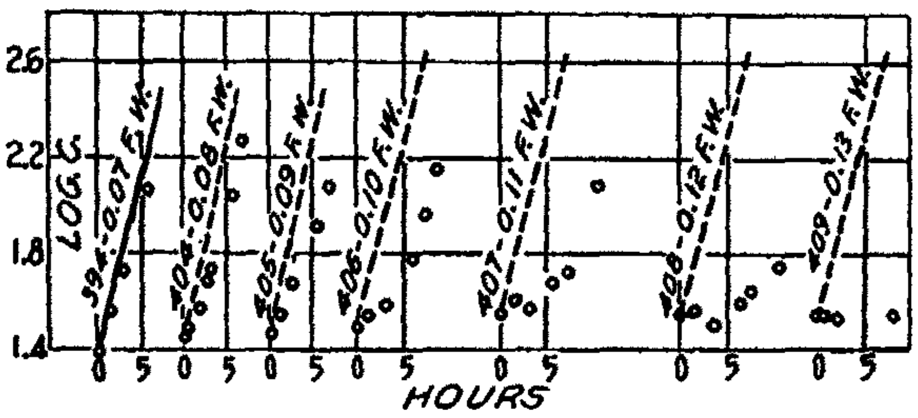

FIG. 8

TABLE XIII (Acetic Acid)

$C_2H_4O_2$ per L	0.00	0.04	0.08	0.10	0.13
P_H	4.03	3.90	3.80	3.76	3.67

In view of these results, the effects produced by the two acids can not be ascribed to the hydrogen-ion concentration, which was about 100 times as great in one solution as in the other; on the other hand, it seemed possible that the acids might be neutralizing and thus rendering inactive the bios in the wort. If this were the case, the same concentration of acid in the culture fluid should prove more harmful if some of the wort were replaced by an equal volume of a solution of sugar and salts. Table XIV gives the results obtained by adding acetic acid to a solution made up of equal volumes of wort and the "artificial medium" used in my experiments on the yield of yeast in diluted wort[1]. As shewn in Fig. 9, the phenomena are the same as those in pure wort; at 0.06 $C_2H_4O_2$ per litre the points are just dropping from the line k = 0.16. The P_H values are slightly less than with pure wort; for 0.08 $C_2H_4O_2$ per litre P_H = 3.69 as against 3.80 (Table XIII). Evidently it is not by destroying the bios that the acids reduce the rate of reproduction.

TABLE XIV (Acetic Acid)

0.00FW		0.02FW		0.04FW		0.06FW	
t	Log C	t	Log C	t	Log C	t	Log C
0.0	1.41	0.0	1.41	0.0	1.41	0.0	1.41
1.0	1.49	1.2	1.46	1.5	1.49	2.0	1.54
4.8	2.26	5.2	2.29	5.4	2.18	5.5	2.16

0.08FW		0.10FW		0.12FW	
0.0	1.41	0.0	1.41	0.0	1.41
2.1	1.45	2.2	1.41	2.5	1.41
5.7	1.99	5.8	1.58	6.0	1.48

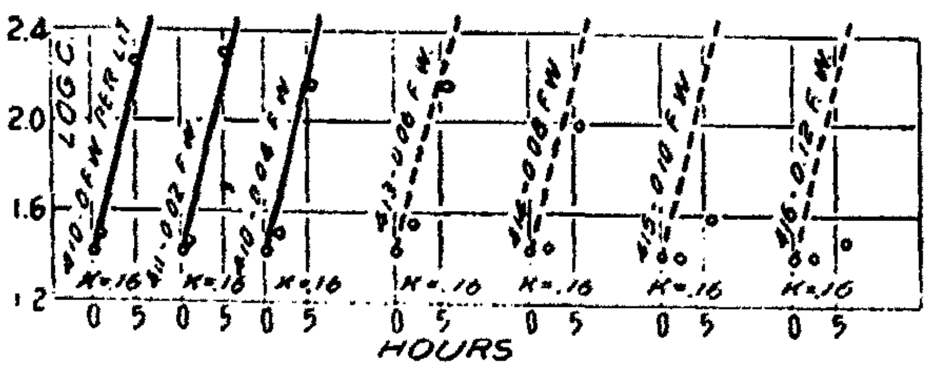

FIG. 9

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[1] J. Phys. Chem. 26, 49 (1922)

Summary

The effect on the rate of reproduction of yeast in wort, produced by adding various amounts of phenol, methyl-green, acetone, sodium bicarbonate, hydrochloric acid or acetic acid has been determined at 25° C.

In general there is a concentration for each poison below which the addition has no influence on the rate; higher concentrations cause an initial pause, followed by slow reproduction.

Absence of reproduction in the poisoned solution does not necessarily imply death of all the cells.

My thanks are due to Prof. W. Lash Miller under whose direction these measurements were carried out, and to Messrs. G. H. W. Lucas and F. Eldon for help in making the counts.

The University of Toronto
May, 1923.

ADSORPTION BY PRECIPITATES. VI.

BY HARRY B. WEISER

Adsorption from Mixtures of Electrolytes; Ionic Antagonism

In a paper published in the Autumn of 1921 was reported the results of a series of experiments dealing with adsorption during the precipitation of colloids by mixtures of electrolytes[1]. The experiments indicated that two factors influenced the precipitating action of mixtures of electrolytes: the effect of the presence of each precipitating ion on the adsorption of the other; and the stabilizing action of the ions having the same charge as the colloid. If the influence of both of these factors was small the precipitation value of mixtures was approximately additive while if the influence of both factors was large the precipitation value was greater than would be expected from the critical values for the separate salts. A year after the publication of my observations, Freundlich and Scholz[2] reported on the results of similar experiments in a paper entitled "Coagulation by Mixtures of Electrolytes". A study was made of the precipitation with various mixtures of electrolytes, of colloidal gold prepared by Donau's method,[3] of colloidal As_2S_3 and of colloidal sulphur prepared by both von Weimarn's method[4] and Oden's method[5].

The results seemed to show that with gold sol and von Weimarn's sulphur sol the action of the precipitating cations showed an additive relationship, while the precipitating action was not additive with As_2S_3 sol and Oden's sulphur sol particularly with mixtures of ions having widely varying precipitating power that are said to be highly hydrated. Since von Weimarn's sulphur sol is not hydrous while Oden's sol is hydrous, Freundlich and Scholz conclude that the hydration of the colloid and of the precipitating ions is of primary importance in producing ionic antagonism and so in determining whether the precipitation values of mixtures shall be additive or above the additive value. They are thus led to believe that As_2S_3 is a hydrophile sol although it is not usually so considered; and finally, they suggest that the behavior of colloids with mixtures is a suitable means of determining to what extent the stability is influenced by hydration. "We believe with Neuscholsz," say Freundlich and Scholz, "that the ionic antagonism observed in a test tube is closely related to the phenomenon which has been recognized as such in the biological action of electrolytes and has been followed by J. Loeb, S. Lillie and others. As an example of this kind of biological action of electrolytes may be mentioned a series of investigations by S. Lillie[6]. The cilia of the larva of a ringworm,

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[1] Weiser: J. Phys. Chem., **25**, 665 (1921)

[2] Kolloidchem. Beihefte, **16**, 267 (1922)

[3] Donau: Monatsh., **26**, 525 (1905)

[4] Von Weimarn and Malyschew: Kolloid-Z., **8**, 214 (1911)

[5] Oden: "Der kolloide Schwefel", (1912)

[6] Lillie: Am. J. Physiol., **10**, 433 (1904)

Arenicola, is liquefied by a solution containing sodium ion: the addition of a small amount of a divalent cation stops this process. At the first glance, our observations seem to be different in certain respects from this kind of biological action of electrolytes and from the ionic antagonism observed by Neuscholsz[1] using lecithin sol. In both of the latter cases it was frequently observed that the action of univalent cations could be nullified by the addition of divalent cations while with sulphur sol the action of divalent cations was decreased under the influence of univalent cations. This is probably only a superficial difference. The coagulation of the sulphur sol is realized only at such concentrations of univalent cations that small concentrations of divalent cations can not annul their influence by displacing their adsorption. If we had studied phenomena like the biological action of electrolytes which could be observed at smaller concentrations of univalent cations, we could have nullified their effect by divalent cations. According to the view arrived at in this paper we believe that in these biological processes as well as in the coagulation of hydrophile sulphur sol, pure electrical influences of pronounced ionic antagonism can not be produced; for ionic antagonism a hydration influence is always necessary, such as appears with increasing strength when we go from gold sol or Weimarn sulphur sol to As_2S_3 sol and finally to hydrophile sulphur sol".

From this account it is evident that Freundlich and Scholz are convinced that the extent of hydration of a colloid is the most important factor in causing the ionic antagonism which results in precipitation values for certain mixtures of electrolytes that are considerably above the additive values. It is a great pity that this conclusion was jumped at from a study of but one sol that appears to belong definitely to the class of hydrophile or hydrous colloids. The conclusions of Freundlich and Scholz would have been more convincing if they had extended their observations to the sols of the hydrous oxides which are quite as representative of the class of hydrophile colloids as is colloidal sulphur. Moreover the preliminary experiments reported in my paper, previously referred to, seemed to indicate that the general conclusions of Freundlich and Scholz were open to question. Accordingly a series of experiments bearing on these points was carried out, with the results recorded in the following section.

EXPERIMENTAL

Experiments with Hydrous Chromic Oxide

Since chromic oxide is very highly hydrous, the colloidal solution of this substance was used in the initial experiments. The positively charged colloid was prepared according to the method of Neidle[2] by dialysis in the hot of the hydrous oxide peptized by chromic chloride. The dialysis was continued for several days until the dialysate contained but a trace of chloride and the pH of the solution was slightly less than that of pure water. The concentration was adjusted to exactly 2 g Cr_2O_3 per liter. The colloid was stored in a pyrex flask and pyrex vessels were used in all experiments.

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[1] Pflüger's Arch., 181, 17 (1920)

[2] J. Am. Chem. Soc., 39, 71 (1907)

Precipitation experiments. The precipitation value of the colloid was determined in the following manner: In one test tube was placed 10 cc of sol and in a second test tube, a suitable amount of electrolyte diluted to 10 cc. The sol was then added rapidly to the electrolyte and the mixture was poured back and forth a number of times. The tube containing the mixture was stoppered and was set aside for exactly 24 hours, after which it was shaken vigorously and centrifuged for 2 minutes at 3000 r.p.m. The presence of complete precipitation was evidenced by the entire absence of color in the supernatant liquid. After getting the approximate precipitation value the exact value was determined by carrying out a series of experiments with electrolyte concentrations that varied not more than 0.01 to 0.02 cc. The sharpness of the value obtained was increased by the long period of standing before examining for complete precipitation.

The precipitation value of mixtures was obtained in the same manner as for single electrolytes, the total volume of the mixture being made up to 10 cc before adding to the colloid. The results of experiments using different pairs of electrolytes of widely varying and of similar precipitating power are given in Tables I, II and III. Instead of expressing the precipitation value in the usual way, I have given simply the number of cubic centimeters of the standard solutions necessary for precipitation in a total volume of 20 cc. In other respects the tables are self-explanatory.

TABLE I

Precipitation of Colloidal Cr_2O_3 with Mixtures of KCl and K_2SO_4

N/2KCl taken cc	N/100 K_2SO_4 to complete coagulation			
	taken cc	calculated cc	difference	
			cc	percent
2.27				
	1.35			
0.5	0.85	1.05	−0.20	−19
1.0	0.65	0.75	−0.10	−13
1.5	0.37	0.45	−0.08	−18
2.0	0.13	0.16	−0.03	−18

TABLE II

Precipitation of Colloidal Cr_2O_3 with Mixtures of KCl and $K_2C_2O_4$

N/2 KCl taken cc	N/100 $K_2C_2O_4$ to complete coagulation			
	taken cc	calculated cc	difference	
			cc	percent
2.27				
	1.50			
0.5	0.92	1.10	−0.18	−16
1.0	0.65	0.79	−0.14	−18
1.5	0.40	0.47	−0.07	−15
2.0	0.14	0.17	−0.03	−18

TABLE III

Precipitation of Colloidal Cr_2O_3 with Mixtures of K_2SO_4 and $K_2C_2O_4$

N/100 K_2SO_4 taken cc	N/100 $K_2C_2O_4$ to complete coagulation			
	taken cc	calculated cc	difference	
			cc	percent
1.35				
	1.40			
0.50	0.86	0.88	−0.02	−2
0.675	0.70	0.70	0.0	0
1.00	0.35	0.36	−0.01	−3

The above results with the highly hydrous chromic oxide are clearly not in accord with the conclusions of Freundlich and Scholz. It will be noted that mixtures of electrolytes having widely different precipitating power such as KCl and K_2SO_4 do not give values considerably above the additive value such as Freundlich and Scholz would predict. On the contrary the values for such mixtures are actually *less* than additive by a quite appreciable amount. Such a result is altogether in accord with what one might expect if the antagonistic action of the precipitating ions was slight at concentrations below the precipitation value of each. From the slope of the usual adsorption isotherm it is clear that adsorption is relatively greater at lower concentrations. The adsorption of Cl′ ion is relatively greater at concentrations below its precipitation value so that relatively less sulphate or oxalate is necessary to bring the combined adsorption above the critical value necessary for neutralization and coagulation. As before stated such a result would follow only in case there is little or no antagonistic action between chloride ion and sulphate or oxalate ion in the sense that the presence of each decreases the adsorption of the other at concentrations below the precipitation value. That such is the case is evident from the results given in the subsequent paragraph.

Adsorption experiments. Adsorption of oxalate ion during the coagulation of colloidal hydrous chromic oxide by mixtures of KCl and $K_2C_2O_4$ was determined both below and above the precipitation value. The procedure was as follows: To 30 cc portions of colloid in a 60 cc bottle were added various mixtures of KCl and $K_2C_2O_4$ made up to 30 cc. After allowing the mixture to stand until the precipitate started to settle out, it was centrifuged for 10 minutes thereby matting the precipitate in the bottom of the bottle. The supernatant liquid was poured off and a 50 cc portion was acidified with H_2SO_4, heated to 70° and titrated with N/50 $KMnO_4$ in the usual way using a 2 cc pipette graduated in tenths of a cc. The results of a series of experiments are given in Table IV.

The first three experiments in Table IV show that a relatively large amount of chloride has no appreciable effect on the adsorption of oxalate below the precipitation value of the latter. A very large excess of chloride decreases measurably the adsorption of oxalate above the precipitation value but it will be noted the adsorption of oxalate is decreased less than 4 percent by the

TABLE IV

Adsorption by Hydrous Chromic Oxide of Oxalate in the Presence of Chloride

Mixtures added to 30 cc colloid containing 0.06 gms. Cr_2O_3			Oxalate adsorbed	
N/2 KCl	N/100 $K_2C_2O_4$	H_2O	cc N/100	Gms per mole Cr_2O_3
4.50	1.35	24.15	1.35	1.505
3.00	1.95	25.05	1.95	2.174
1.50	2.85	25.65	2.85	3.177
0.00	4.20	25.80	4.20	4.682
0.00	8.50	21.50	7.34	8.182
21.50	8.50	0.00	6.66	7.424
0.00	12.00	18.00	9.42	10.500
18.00	12.00	0.00	8.83	9.842
0.00	15.00	15.00	11.10	12.373
15.00	15.00	0.00	10.68	11.905
0.00	20.00	10.00	12.46	13.889
10.00	20.00	0.00	12.35	13.667

presence of 50 times its concentration of chloride (Exp. 7) and less than 1 per cent by 25 times its concentration of chloride (Exp. 8). In the light of these observations it is evident that the relatively high precipitation value of KCl is due to weak adsorption of chloride ion associated with but slight adsorption of the stabilizing potassium ion.

Experiments with Colloidal Stannic Oxide

While the results with colloidal chromic oxide furnish fairly conclusive evidence that a concentration far above the additive value is not necessarily required to precipitate a highly hydrous colloid with mixtures of electrolytes having widely varying precipitating power, still it seemed desirable to make additional observations on a negative colloid using electrolytes with cations that are supposedly highly hydrated, as Freundlich did. For this purpose the highly hydrous colloidal stannic oxide prepared by Zsigmondy's method[1] was employed and precipitations were made with mixtures of the chlorides of lithium and barium and of lithium and magnesium. The method of procedure was identical with that described above for colloidal chromic oxide. After allowing to stand 24 hours and centrifuging, the supernatant liquid was tested for complete precipitation by adding an excess of $BaCl_2$. The absence of a trace of gelatinous precipitate on standing indicated complete coagulation. The results are given in Tables V and VI. The colloid contained 7.6 g SnO_2 per liter.

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[1] Zsigmondy: Ann., **301**, 361 (1898)

TABLE V

Precipitation of Colloidal SnO$_2$ with Mixtures of LiCl and BaCl$_2$

N/10 LiCl taken cc	N/100 BaCl$_2$ to complete coagulation			
	taken	calculated	difference	
	cc	cc	cc	percent
5.10				
	3.10			
1.00	2.25	2.50	−25	−10
2.50	1.35	1.58	−23	−15
4.00	0.55	0.67	−12	−18

TABLE VI

Precipitation of Colloidal SnO$_2$ with Mixtures of LiCl and MgCl$_2$

N/10 LiCl taken cc	N/100 MgCl$_2$ to complete coagulation			
	taken	calculated	difference	
	cc	cc	cc	percent
5.10				
	3.35			
2.00	1.98	2.04	−0.06	−3
3.50	1.00	1.06	−0.06	−6

The observations with hydrous stannic oxide merely confirm the results with chromic oxide. Here again the precipitation values of mixtures of univalent and bivalent precipitating ions of varying degrees of hydration are appreciably less than the additive values. The results are so nearly in line with those obtained with hydrous chromic oxide that there is doubtless little if any antagonistic action between the precipitating cations below the precipitation value of each.

Experiments with Colloidal Arsenious Sulphide

From our earlier observations with arsenious sulphide sol it was known that there is an appreciable antagonistic action bewteen electrolytes containing univalent and bivalent precipitating cations in the sense that relatively more of each must be used to cause precipitation in case the other is also present in the solution. Since arsenious sulphide sol is usually classed as a hydrophobe colloid and since the pairs of ions employed (K with Ba or Sr) are said to be but slightly hydrated, it is difficult to reconcile our observations with the view that ionic antagonism is a result chiefly of high hydration of the colloid and the precipitating ions. This view seems all the more improbable since the results with highly hydrated colloids using hydrated precipitating ions, show a tendency opposite to those with arsenious sulphide. To explain our earlier results with As$_2$S$_3$ we assumed that the adsorption of Ba$^{\cdot\cdot}$ ion, say, was decreased appreciably by the presence of K$^{\cdot}$ ion below the precipitation value so that a higher concentration of the former was required to cause the adsorption necessary for neutralization when the latter was present. Freundlich would reject this explanation on the ground that KCl precipitates only in high concentrations indicating such a low adsorption of K˙ ion that the presence of the latter in concentrations below the precipitation value can have no appreciable influence on the adsorption of Ba˙˙ ion. The weak point in this argument is that a high precipitation value for an electrolyte does not necessarily indicate very low adsorption of the precipitating ion[1]. This is true only in case the adsorption of the stabilizing ion is relatively slight. In the case under consideration the adsorption of K˙ ion may be fairly large, but in spite of this, a high concentration of KCl may be necessary since the adsorption of Cl′ ion at certain concentrations below the precipitation concentration may be comparable to that of K˙ ion. It is thus a question of fact, whether the adsorption of K˙ ion by colloidal As_2S_3 below the precipitation value is or is not sufficiently great to influence appreciably the adsorption of Ba˙˙ ion. This problem is dealt with in the subsequent experiments.

Precipitation experiments. Colloidal As_2S_3 was prepared by dropping slowly a solution of As_2O_3 saturated at 30° into H_2S water through which was bubbled continuously a stream of H_2S, purified by passing through three wash-bottles containing water. The excess H_2S was washed out by bubbling a stream of hydrogen through the solution after which the latter was filtered into a dark glass bottle. Approximately four liters of colloid containing 22.3 g per liter were prepared. It was necessary to have a colloid that was fairly strong in order to get sufficient adsorbent in a reasonable volume. The colloid was kept in an atmosphere of hydrogen in a dark bottle. To do this the space above the liquid in the bottle was filled with hydrogen and after inserting the stopper the bottle was inverted thus preventing the escape of the gas.

Precipitation values were carried out in much the same manner as for the hydrous colloids except that the time of standing after mixing with electrolyte was decreased to 2.5 hours. The mixture was shaken after the first and second hour and again at the conclusion of the 2.5 hour interval. Since the precipitation value of mixtures was the same whether the electrolytes were added separately or together, the latter process was followed as in the previous cases[2]. To test whether precipitation was complete, the supernatant liquid was filtered into a test tube and examined for the presence or absence of the greenish opalescence that characterizes the very dilute colloid. Since KCl with $BaCl_2$ or $SrCl_2$ was used in our earlier experiments it seemed desirable to use different pairs of electrolytes in this work. The results in Tables VII, VIII, IX and X were obtained with mixtures of LiCl and $BaCl_2$, LiCl and $MgCl_2$, $BaCl_2$ and $MgCl_2$, HCl and $MgCl_2$.

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[1] Weiser: J. Phys. Chem., **25**, 680 (1921)

[2] Cf. Freundlich and Scholz: Kolloidchem. Beihefte., **16**, 281 (1922)

TABLE VII

Precipitation of Colloidal As_2S_3 with Mixtures of LiCl and $BaCl_2$

N/2 LiCl taken cc	N/100 $BaCl_2$ to complete coagulation			
	taken	calculated	difference	
	cc	cc	cc	percent
4.05				
	4.03			
0.5	4.50	3.54	0.96	27
1.0	4.25	3.03	1.22	38
2.0	3.76	2.03	1.73	84
3.0	2.25	1.03	1.22	118

TABLE VIII

Precipitation of Colloidal As_2S_3 with Mixtures of LiCl and $MgCl_2$

N/2 LiCl taken cc	N/100 $MgCl_2$ to complete coagulation			
	taken	calculated	difference	
	cc	cc	cc	percent
4.05				
	4.35			
0.5	5.15	3.81	1.34	35
1.0	5.20	3.27	1.93	59
2.0	4.25	2.20	2.05	93
3.0	2.25	1.13	1.42	126

TABLE IX

Precipitation of Colloidal As_2S_3 with Mixtures of $BaCl_2$ and $MgCl_2$

N/100 $BaCl_2$ taken cc	N/100 $MgCl_2$ to complete coagulation			
	taken	calculated	difference	
	cc	cc	cc	percent
4.03				
	4.35			
2.00	2.20	2.19	0.01	0.5
3.00	1.15	1.11	0.04	4.0

TABLE X

Precipitation of Colloidal As_2S_3 with Mixtures of HCl and $MgCl_2$

N/5 HCl taken cc	N/100 $MgCl_2$ to complete coagulation			
	taken	calculated	difference	
	cc	cc	cc	percent
4.75				
	4.35			
1.0	4.65	3.83	0.82	22
2.0	4.45	2.92	1.53	52
3.0	3.35	2.00	1.35	68
4.0	2.00	1.08	0.92	85

As observed in the case of hydrous chromic and stannic oxides the precipitation value of mixtures is almost additive in case the precipitating power of each is similar (Table IX). On the other hand, with the mixtures containing both a univalent and bivalent precipitating ion there is a wide variation from the additive value as indicated in Tables VII, VIII and X.

Adsorption Experiments. Since the quantitative estimation of barium can be made with a high degree of accuracy, a study was made of the effect of lithium on the adsorption of barium at the precipitation concentration of various mixtures of the chlorides of the metals. The procedure was as follows: 125 cc of colloid containing 2.84 g As_2S_3 was precipitated in a wide mouth bottle with the precipitation concentration of electrolyte or electrolytes as given in Table VII. The total volume was 250 cc. After allowing to stand 2.5 hours the mixture was centrifuged 10 minutes at 3000 r.p.m. and 200 cc of the supernatant liquid was removed for analysis. This solution was first acidified with HCl and allowed to stand for 24 hours. As the concentration of electrolytes was so near the precipitation value, there was always a trace of As_2S_3 that settled out after the acidified solution had stood over night. This was filtered off, after which the solution was heated to boiling and the barium precipitated with an excess of H_2SO_4. To render the results of a series of experiments comparable it was necessary to add the required amount of LiCl or LiCl and $MgCl_2$ to the solution that was free from it originally. It goes without saying that the volume of solution and the amount of precipitant were kept constant.

TABLE XI

Adsorption by Arsenious Sulphide of Barium in the Presence of Lithium

Mixtures added to 125 cc of colloid containing 2.84 g As_2S_3			BaSO4 remaining in 200 cc		Barium adsorbed	
N/2 LiCl	N/100 $BaCl_2$	H_2O		Average	gms	gms per mole As_2S_3
0	50.80	74.20	0.0288	0.0284	0.0140	1.214
0	50.80	74.20	0.0280			
0	56.25	68.75	0.0316	0.0319	0.0151	1.310
0	56.25	68.75	0.0322			
6.25	56.25	62.50	0.0371	0.0373	0.0112	0.971
6.25	56.25	62.50	0.0375			
0	53.10	71.90	0.0304	0.0302	0.0143	1.250
0	53.10	71.90	0.0301			
12.5	53.10	59.40	0.0363	0.0365	0.0097	0.841
12.5	53.10	59.40	0.0368			
0	47.00*	73.00	0.0259	0.0260	0.0132	1.145
0	47.00	73.00	0.0260		0	
25.0	47.00*	48.00	0.0358	0.0357	0.0600	0.520
25.0	47.00	48.00	0.0355			

* +5 cc $MgCl_2$

Experiment 1 gives the adsorption of Ba·· ion at the precipitation concentration for $BaCl_2$; experiments 2, 3 and 4 give (a) the adsorption of Ba·· ion from $BaCl_2$ alone at the concentration necessary to cause precipitation from the mixture with LiCl and (b) the adsorption of Ba·· ion in the presence of Li· ion. In experiment 4 the concentration of $BaCl_2$ is below the precipitation value, necessitating the addition of some $MgCl_2$. Since the precipitating power of these two salts is very nearly the same, the presence of the small amount of Mg·· ion can have little or no effect on the adsorption of Ba·· ion at this concentration. Attention should be called to the fact that the concentrations of LiCl and $BaCl_2$ used in experiments 2, 3 and 4 correspond to those for 0.5, 1.0 and 2.0 cc of LiCl, respectively, in Table VII. The results are given in detail in Table XI.

The observations recorded in Table XI show conclusively that concentrations of lithium below the precipitation value have a marked effect on the adsorption of barium. Thus at the precipitation concentration of a mixture containing one-eighth the precipitation value of LiCl alone the adsorption of Ba·· ion is lowered more than 25 percent; while from a mixture containing one-half the precipitation value of LiCl alone, the adsorption of Ba·· is decreased 53 percent. This marked effect of Li· ion in concentrations below the precipitation value on the adsorption by As_2S_3 of the strongly adsorbed Ba·· ion is thus a factor of primary importance in raising the precipitation value of $BaCl_2$ in the presence of LiCl. The high precipitation value of LiCl cannot be due to very low adsorption of Li· ion which would displace but little Ba·· ion at concentrations below the precipitation value; but is due to fairly marked adsorption of Li· ion associated with appreciable adsorption of the stabilizing Cl′ ion within the concentration limits investigated. While the adsorption of the stabilizing ion of an electrolyte is usually disregarded since in many cases the effect is small compared to that of the precipitating ion, the time-honored statement is certainly incorrect that only the anions of an electrolyte determine its precipitation value for a positive colloid and only the cations for a negative colloid. Indeed it is not improbable in the case at hand that at certain concentrations of LiCl or KCl below the precipitation value, the adsorption of Cl′ ion is actually greater than that of the cation, particularly in the presence of a divalent ion such as Ba·· ion[1].

Another possible interpretation of the high precipitation value of LiCl is that neutralization is compensated for in part by a hydration influence which tends to stabilize the colloid. This hypothesis is untenable since the precipitation value of NaCl is almost as high as of LiCl and that of KCl is of the same order of magnitude although Na· and K· ions are said to be hydrated much less than Li· ion. A further objection to this hypothesis is that the relative degree of hydration of the ions is still largely a matter of conjecture. In discussing this paper at the Milwaukee meeting Professor Bancroft called attention to the results of some recent investigations of Baborovsky[2] which seemed

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[1] Cf. Weiser: Loc. cit.

[2] Rec. trav. chim. (4) 4, 229 (1923)

to reverse the usually accepted order of hydration of the ions. Until we have more definite information on this point it would seem to be a waste of time to attempt to establish some relationship between the stability of a colloid and the hydration of an adsorbed ion.

Returning to Table VII and VIII it will be noted that LiCl has a more marked effect on the precipitation value of $MgCl_2$ than of $BaCl_2$. This is exactly what one should expect in view of the fact that the adsorption of $Mg^{\cdot\cdot}$ ion is not so great as that of $Ba^{\cdot\cdot}$ ion as evidenced by the higher precipitation value of $MgCl_2$. However, the variation for mixtures is less marked than that observed by Freundlich and Scholz. Referring to their observations the latter investigators say: "From the standpoint of the effect of hydration it is not at all surprising that the peptizing action of $Li^{\cdot}$ ion stabilizes the solution to a different degree against cations of the same valence. The coagulation value of $Mg^{\cdot\cdot}$ ion is much greater than that of $Ba^{\cdot\cdot}$ ion in a solution containing LiCl although $Mg^{\cdot\cdot}$ and $Ba^{\cdot\cdot}$ ions have almost the same coagulating power in pure solution." Unfortunately Freundlich and Scholz seem to have overlooked the fact that small differences in precipitation value do not necessarily mean small percentage differences. As a matter of fact they found the precipitation value of $MgCl_2$ to be 20 percent greater than that of $BaCl_2$ a difference that is certainly not negligible. Indeed the percentage difference between the precipitation values of LiCl and KCl was found to be no greater; yet this was clearly recognized as a difference because the actual figures representing the precipitation values were larger. As our figures show, the difference between the precipitation values of $MgCl_2$ and $BaCl_2$ is but seven percent as compared with twenty percent observed by Freundlich and Scholz. This is doubtless the chief cause of the variation between Freundlich's values and our own in the precipitation with mixtures. The percentage difference in precipitation value of pure electrolytes is not the same on account of the wide difference in the concentration of the sols. Freundlich and Scholz used a very dilute sol, 0.4 g As_2S_3 per liter, for some unknown reason, while we employed a fairly concentrated sol for the reason already given. That the curves representing the precipitation values of ions diverge more markedly the greater the dilution has been demonstrated and an explanation offered in a recent paper from this laboratory[1]. In case adsorption studies are not contemplated one would ordinarily not employ such a strong As_2S_3 sol as we have used for obtaining precipitation data. On the other hand there seems no good reason for working with an As_2S_3 sol as dilute as 0.04 percent, particularly since it is difficult to get accurate precipitation data with a sol of this concentration. This may, account for the approximate values frequently given in Freundlich and Scholz's tables.

Comparing the results in Tables VIII and X it will be seen that slightly more $MgCl_2$ is necessary to complete coagulation of the sol in the presence of LiCl than of HCl. This is readily explained when we consider that two factors enter into a comparison of this sort; the neutralizing action of the adsorbed

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[1] Weiser and Nicholas: J. Phys. Chem., 25, 742 (1921)

Li˙ ion or H˙ ion and the antagonistic effect of the presence of these ions on the adsorption of Mg˙˙ ion. On account of its greater adsorption, the antagonistic action is greater than that of Li˙ but so is its precipitating power: the net result is that a somewhat smaller concentration of Mg˙˙ ion is necessary to bring about precipitation in the presence of H˙ ion than of Li˙ ion.

The results given in Table X are interesting from another point of view. Tartar[1] and his pupils have recently put forth the view that the precipitation value of all electrolytes for colloids is approximately the same at the same hydrogen ion concentration. This can not be even approximately true in the case cited. The precipitation value of $MgCl_2$ may be the same at relatively enormous differences in the hydrogen ion concentration. As already pointed out the effect of difference in the H˙ ion concentration on the precipitation values of another cation for colloidal As_2S_3 is determined by the relative adsorbability of the two ions and by the effect of the presence of variable amounts of each on the adsorption of the other.

Summary and Conclusions

1. The precipitation values of mixtures of pairs of electrolytes of similar and widely varying precipitating power have been found for positive hydrous chromic oxide sol and for negative hydrous stannic oxide sol and arsenious sulphide sol; and the adsorption of certain ions from mixtures of electrolytes during the precipitation of sols has been determined.

2. The precipitation value of an electrolyte for a colloid is that concentration which results in sufficient adsorption of the precipitating ion to neutralize the combined adsorption of the original stabilizing ion and the stabilizing ion added with the electrolyte. The adsorption of the stabilizing ion varies widely but is never negligible if the electrolytes precipitate only in high concentration as is usual with electrolytes having univalent precipitating ions.

3. The precipitation values of mixtures of electrolytes of similar precipitating power show an approximately additive relationship because the "ionic antagonism" between the precipitating ions is not marked.

4. The precipitating values of mixtures of pairs of electrolytes of widely varying precipitating power and of different degrees of hydration may be less than the additive values. Thus mixtures of KCl and either K_2SO_4 or $K_2C_2O_4$ precipitate hydrous chromic oxide at concentrations less than the additive values; and the same is true for mixtures of LiCl and either $BaCl_2$ or $MgCl_2$ with hydrous stannic oxide.

5. A study of the effect of chloride ion on the adsorption of oxalate ion both above and below the precipitation concentration of the latter discloses the absence of any marked ionic antagonism. The high precipitation value of KCl for hydrous chromic oxide is thus due to weak adsorption of chloride ion associated with but slight adsorption of the stabilizing potassium ion. The

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[1] Tartar and Gailey: J. Am. Chem. Soc., 44, 2212 (1922); A supplementary report was read at the Milwaukee meeting of the American Chemical Society.

absence of appreciable ionic antagonism accounts for the precipitation concentrations of mixtures not rising above the additive values in the several cases referred to in (4). That the precipitation values in these cases are lower than the additive values is accounted for by the well known fact that adsorption is proportionately greater at lower concentrations of the adsorbed ion. Thus the adsorption of chloride ion is relatively greater at concentrations well below its precipitation value so that relatively less sulphate or oxalate ion is necessary to bring the combined adsorption above the critical value necessary for neutralization and coagulation.

6. The results given in (4) and (5) are not in accord with the conclusions of Freundlich and Scholz that the hydration of a colloid and of the precipitating ions is of primary importance in producing ionic antagonism and that the behavior of a colloid with mixtures may furnish a suitable means of distinguishing a hydrophobe from a hydrophile colloid.

7. The precipitation values of mixtures of electrolytes that vary widely in their precipitating power may be much greater than the additive values. This was observed on As_2S_3 sol using mixtures of LiCl with either $BaCl_2$ or $MgCl_2$ and mixtures of HCl and $MgCl_2$.

8. The adsorption of barium ion is decreased to a marked degree by the presence of lithium below the precipitation concentration of the chlorides of the metals. The adsorption of lithium ion is also influenced by the presence of barium ion. This cationic antagonism is the important factor in raising the precipitation concentrations of certain mixtures above the additive values.

9. The high precipitation value of alkali chlorides for colloidal As_2S_3 is not due to very weak adsorption of the cation but results from fairly strong adsorption of the cation associated with appreciable adsorption of the anion. This accounts at once for the high precipitation values of alkali chlorides and for the displacing power of alkali cations.

10 The precipitation value of magnesium chloride is increased more than that of barium chloride in the presence of the same amount of lithium chloride. This is not due primarily to the difference in the hydration of the precipitating ions but results for the most part from stronger adsorption of barium ion than of magnesium ion.

11. The influence of the hydrogen ion concentration on the precipitation values of another cation for colloidal As_2S_3 is determined by the relative adsorbability of the two ions and by the effect of the presence of variable amount of each on the adsorption of the other. It is thus possible to have the same precipitation value for a given electrolyte at widely different hydrogen ion concentrations.

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THE EQUILIBRIUM BETWEEN IODINE AND BARIUM IODIDE IN AQUEOUS SOLUTIONS

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Since the discovery of the fact that iodine dissolves more readily in aqueous solutions of metallic iodides than in pure water the nature of the equilibria existing in these systems has been the subject of numerous investigations. That a compound is formed between the iodine and the iodide is generally accepted. Although the literature covering these investigations is extensive in scope, reference will be made only to those articles which bear directly upon the present work.

Jakowkin[1] was the first to make a systematic study of the equilibria involved. He assumed the reaction: $MI+I_2=MI \cdot I_2$, and he has calculated the corresponding equilibrium constants by means of the relation,

$$K=\frac{C_{MI} \cdot C_{I_2}}{C_{MI_3}} \quad .$$

In the case of barium iodide Jakowkin assumed that both iodine atoms of the salt are equally active in combining with the dissolved iodine and he has based his calculations upon the reaction represented by the equilibrium,

$$1/2BaI_6=1/2BaI_2+I_2 \ .$$

The corresponding equilibrium constant is given by the relation:

$$K=\frac{[2a-(b-x)]x}{b-x},$$

where *a* is the original concentration of the barium iodide, *b* is the total concentration of the iodine as determined by titration and *x* is the concentration of the free uncombined iodine, all in moles per liter in the water layer. For equivalent concentrations of the iodides studied Jakowkin has found that at 25° the equilibrium constants thus calculated are approximately equal to 0.0014.

Herz and Kurzer[2] also have carried out a short series of determinations, using different concentrations of iodine with only one concentration of the salt. They assumed that only one of the two iodine atoms of barium iodide combines with iodine and they have based their calculations upon the equilibrium: $BaI_4=BaI_2+I_2$. The expression representing this equilibrium is,

$$K=\frac{[a-(b-x)]x}{b-x}.$$

The values of K thus calculated show a fair degree of constancy over the range of iodine concentration studied.

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[1] Jakowkin: Z. physik. Chem., 13, 539 (1894); 20, 19 (1896).

[2] Herz and Kurzer: Z. Elektrochem., 16, 869 (1910).

The most recent work on the study of iodine-polyiodide equilibria is that of Van Name and Brown[1]. They have investigated the iodides of zinc, strontium, nickel, cadmium, mercury and lanthanum, and they have recalculated the data of Herz and Kurzer for barium iodide, using the method of Jakowkin. They conclude that the constant calculated by Jakowkin, rather than that of Herz and Kurzer, holds in general not only for the iodides of the bivalent metals, but also for the iodide of the trivalent metal lanthanum.

In a series of papers Van Name and his co-workers[2] report the results of a study of the rate of reaction of metals with halogens dissolved in aqueous solutions of metallic halides. They found that the rate of reaction of metals with a given solution of a halogen, e.g., iodine dissolved in a solution of potassium iodide, is independent of the nature of the metal and depends only on the rate of diffusion of the iodine to the metal. This is in harmony with the diffusion theory of heterogeneous reactions. Moreover, the rate of reaction was found to be markedly increased by increasing the concentration of the potassium iodide.

In a study of the rate of diffusion of iodine in solutions of potassium iodide Edgar and Diggs[3] have found that the rate of diffusion increases with the concentration of potassium iodide and, furthermore, that the increase is distinctly of the same order of magnitude as the increase in the velocity constants for the reaction between the metals and dissolved iodine. Believing that an increase in the potassium iodide concentration may increase the rate of diffusion of iodine indirectly, i.e., by influencing the fluidity, they determined the rate of diffusion of iodine in and the fluidity of solutions over a wide range of potassium iodide concentration. They found that the increase in the rate of diffusion is much too great to be accounted for by the increase in fluidity alone. They assume that KI_3 molecules are present and that these molecules diffuse more slowly than the I_3^- ion. Since an increase in the potassium iodide concentration must repress the ionization of the KI_3, the rate of diffusion of the iodine for this reason decrease as the concentration of the potassium iodide is increased. No satisfactory explanation for the influence of the salt on the diffusion of iodine was found.

It seems very probable that these authors have overlooked one possible and plausible explanation of the mechanism of the process whereby the rate of diffusion of iodine may be increased by increasing the concentration of the potassium iodide. If we consider a potassium iodide solution containing dissolved iodine in contact with an equivalent solution of the potassium iodide alone, diffusion of iodine may take place in two ways. (1) Owing to the difference in concentration of the KI_3 molecules and their ions (K^+ and I_3^-)in the contiguous phases these species will diffuse from higher to lower concentration. Obviously, at the same time KI molecules and their ions will diffuse in the opposite direction. (2) At the same time iodine may be transferred by a

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[1] Van Name and Brown: Am. J. Sci., 44, 105 (1917).

[2] Van Name and co-workers: Ibid., 29, 237; 32, 207.

[3] Edgar and Diggs: J. Am. Chem. Soc., 38, 253 (1916).

second process. Suppose a molecule of iodine, I_2, temporarily free, diffuses from left to right, thus

$$I_2 \longrightarrow I^- \longrightarrow I^- \cdot I_2 \longrightarrow I^- \longrightarrow I_2 \ .$$

When it comes in contact with an I^- ion, or with a KI molecule, it will combine with this to form the tri-iodide ion, or molecule. This in turn may again dissociate and liberate free I_2 to be taken up by succeeding I^- ions or KI molecules. As a homely illustration of the process meant we need but recall the old-fashioned bucket brigade in action at a fire. The iodine molecules may be likened to the buckets which are passed on from man to man. Thus, the distance passed over in the diffusion process in a given time has been increased by the diameter of the I^- ion or KI molecules. Incidentally the actual rate of transfer of KI molecules and I^- ions in the opposite direction has been increased by this transfer of iodine. The polyiodides are relatively unstable. Hence there is always some free iodine in the solution and the interchange of iodine molecules between molecules of KI or I^- ions within the solution will become easier and more frequent as the concentration of the potassium iodide is increased. Excepting for possible differences in fluidity, the rate of diffusion of iodine of a given concentration should be the same in any given concentration of any alkali iodide. The general direction and velocity of the diffusion process will be governed by the concentration gradient of the polyiodide.

In a study of the system, potassium iodide-iodine-alcohol-water, Parsons and Corliss[1] conclude, from phase rule considerations, that no solid polyiodides are formed and that probably no polyiodides exist in solution. While experience teaches that the solubility of iodine in alcohol is decreased by the addition of water and that the solubility of potassium iodide in water is decreased by the addition of alcohol they find that the solubility of iodine and potassium iodide together is nearly the same in 40% or 60% alcoholic solutions as in pure alcohol or pure water. They believe that the increase is solubility is due to the mutual solvent effect of the iodine and potassium iodide on each other. They state that "the mutual solubility of the potassium iodide and iodine increases in proportion to the amount of the other present". As proof of the nonexistence of polyiodides these authors offer the results of a few diffusion experiments in which an agar cup separates a solution of potassium iodide from a second solution of this salt saturated with iodine. They assume that the ions diffuse through the agar at the same rate as through the solvent. While this may be true for very dilute agar sols it is not necessarily true for solid emulsoids, and the specific effect on the diffusion speeds will be different for different ions. Furthermore, their agar cup walls were about 11 mm. thick and were made by dissolving agar in an 0.1 N solution of potassium iodide. Obviously, the actual concentration of the salt in the free water of the solid agar is greater than 0.1 N because of the water taken up by the agar on swelling. Hence, because of unequal osmotic pressures, when this agar membrane is placed in an 0.1 N KI solution water will either pass into the agar or potassium iodide will pass into the solution. For the purposes of this discussion it will be neces-

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[1] Parsons and Corliss: J. Am. Chem. Soc., 32, 1637 (1910).

sary to review briefly the experiments performed by Parsons and Corliss. In the first experiment a 0.16 N solution of potassium iodide saturated with iodine was placed in the cup and the whole then immersed in an 0.1 N solution of the salt. According to the authors, "if the tri-iodide is formed, as shown by Jakowkin and others, the initial condition of the two solutions will be

	Outer solution		Inner solution
(A)	0.1 N KI	agar KI	0.08 N KI 0.08 N KI_3 0.0013 N I_2

and the KI will diffuse from left to right. If, however, no compound is formed, the initial condition will be

	Outer solution		Inner Solution
(B)	0.1 N KI	agar KI	0.16 N KI 0.0813 N I_2

and KI will diffuse from right to left."

They did find that an appreciable amount of KI did diffuse into the 0.1 N solution ahead of any iodine, and hence concluded from this that no polyiodide is formed. Another experiment apparently confirming this was arranged in which an 0.1 N solution of potassium iodide surrounded the cup containing a similar solution saturated with iodine, thus

	Outer solution		Inner solution
(C)	0.1 N KI	agar KI	0.05 N KI 0.05 N KI_3 0.0013 N I_2

"If a compound is formed KI should pass from left to right. But if no compound is formed then we should have as the initial conditions,"

	Outer solution		Inner solution
(D)	0.1 N KI	agar KI	0.1 N KI 0.0513 N I_2

and the concentrations of the potassium iodide being equal at the start they should remain so during the diffusion of the iodine. This they actually found to be the case. Hence they reasoned that the iodine is free and uncombined. It is obvious at a glance that they are basing their conclusions solely upon the relative concentrations of the potassium iodide as indicated in the initially chosen conditions.

It will be interesting to observe that the results obtained are exactly what one might predict on the assumption of the existence of polyiodides. Let us consider the cases (A) and (C) only. In respect to the I^- ion the outer solution is in each case hypertonic to the inner solution, and for this reason the salt should diffuse from left to right as Parsons and Corliss have assumed. Let us now take case (A). Both KI and KI_3 are strong electrolytes and hence at the dilutions used they are highly dissociated. As a rough approximation we may consider them as completely dissociated without vitiating the argument. The difference in concentration of the K^+ ion is roughly 0.06 N, that of the

I^- ion is about 0.02 N and that of the I_3^- ion 0.08 N. These differences in concentration of the respective ions represent the diffusion pressure gradients of the ions, the dominating pressure gradient being that of the potassium ion. Under these conditions the K^+ and I_3^- ions must diffuse into the outer solution. The dissociated ions from a molecule electrostatically attract each other; the speed of the slower moving ion is accelerated by that of the faster, and vice versa. The velocities of the K^+ and I^- ions are approximately equal, that of the I_3^- is less. Therefore, in diffusing the K^+ ions will drag with them both I^- and I_3^- ions, and possibly more of the faster moving I^- ion than of the I_3^- ion. The concentration of the I^- ion thus increased in the outer solution later adjusts itself to an isotonic condition by diffusing into the cup, accompanied simultaneously by the outward diffusion of I_3^- ions and the outward transference of iodine by the process described above. In case (C) the inner and outer solutions are initially isotonic with respect to the K^+ ions; the concentration gradients of the I^- and I_3^- ions are equal and opposite. The I_3^- ions and the I_2, by secondary diffusion, diffuse outward; the I^- ions diffuse to the inner solution and the extent of this latter diffusion is less than it would be normally by the number of I^- ions set free in the secondary diffusion of iodine. It is obvious therefore that the conclusions of Parsons and Corliss regarding the nonexistence of polyiodides in solution are entirely untenable.

In the previous work upon this subject the concentrations for the most part have been expressed in gram-mols, or gram-equivalents, per liter of solution. It is evident that if very large concentration ranges are used there will be a considerable variation in the amount of solvent present. When the results for the different concentrations are compared on this basis the explanation of any variations in the equilibria observed must take into consideration not only the concentration of the iodide and the iodine, but also of the solvent present. The present work was undertaken with the purpose of eliminating effects due to variation in the amount of solvent by expressing all concentrations in gram-mols per 1000 g. of solvent.

Purification of Materials

Barium Iodide. The pure salt which had been twice recrystallized from a solution containing hydriodic acid was mixed with a small quantity of freshly prepared solid ammonium iodide and fused in a stream of dry nitrogen. The resulting product is a white crystalline solid which can be kept indefinitely over phosphorus pentoxide. The purity of the salt was tested by repeated accurate determinations of both the iodine and the barium content.

Iodine. Baker's resublimed iodine was sublimed once from an intimate mixture with pure solid potassium iodide and once alone. All iodine determinations were made with an approximately 0.04 N solution of pure sodium thiosulphate which was frequently standardized against a freshly prepared iodine solution. This in turn was previously checked against a solution of sodium arsenite made from resublimed arsenic trioxide.

Carbon Tetrachloride. A large sample of this solvent was washed with water containing a small amount of sodium hydroxide. It was then repeatedly washed with pure water and allowed to stand over solid ahhydrous calcium chloride. Before use the solvent was decanted and redistilled.

Solubility of Iodine in Water

The solubility of iodine in water at 25° was determined by shaking an excess of pure iodine with conductivity water in tightly stoppered bottles of Jena glass. These were rotated in a large thermostat until equilibrium was established. Samples were withdrawn by means of accurately calibrated pipettes and run into tared glass stoppered erlenmeyer flasks containing a solution of potassium iodide, and quickly weighed. The exact weight of the iodine solution was determined by difference and the iodine titrated with the thiosulphate solution. The solubility was calculated in mols of iodine dissolved in 1000 g. of water. Six successive determinations gave the following values: 0.0013291, 0.0013295, 0.0013287, 0.0013294, 0.0013292, 0.0013296. The mean value, viz., 0.001329, agrees well with the value of 0.00132 obtained by Bray and MacKay[1] for mols of iodine in 1000 c.c. of a saturated water solution.

The Distribution of Iodine between Carbon Tetrachloride and Water

In making these determinations carbon tetrachloride, conductivity water and solid iodine were placed in glass-stoppered bottles, carefully sealed and then rotated in the thermostat at 25° until the iodine was completely dissolved and the distribution equilibrium was attained. 25 c.c. portions of the water layer and 10 c.c. portions of the carbon tetrachloride layer were quickly transferred without loss of iodine or solvent to tared glass-stoppered flasks containing an excess of a strong solution of potassium iodide and then quickly weighed. The iodine was determined by titration and the weights of the solvents by difference. From the data obtained the distribution ratio was calculated on the basis of 1000 g. of each solvent. This constant is not to be confused with the constant as determined by Linhart[2] on the basis of 1000 g. of saturated solution. He found for K the value 56.75.

The results of these determinations are given in Table I. The constancy of the ratios is all that can be expected when one considers the extremely low concentrations of the iodine in the water layer and also the fact that slight errors are considerably multiplied in reducing concentrations to mols per 1000 g. of solvent.

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[1] Bray and MacKay: J. Am. Chem. Soc., **32**, 914 (1910).

[2] Linhart: J. Am. Chem. Soc., **40**, 158 (1918).

TABLE I

The Distribution of Iodine between Water and Carbon Tetrachloride.

$\frac{\text{Grams } I_2}{1000 \text{ g. } H_2O}$	$\frac{\text{Grams } I_2}{1000 \text{ g. } CCl_4}$	$\frac{I_2 (1000 \text{ g. } CCl_4)}{I_2 (1000 \text{ g. } H_2O)}$	$\frac{I_2 (1000 \text{ c.c. } CCl_4)}{I_2 (1000 \text{ c.c. } H_2O)}$
0.0745	3.8990	52.35	82.60
0.1020	5.3584	52.53	82.62
0.1078	5.6775	52.64	82.86
0.1432	7.5145	52.49	82.69
0.2432	12.6950	52.21	82.37
	Mean	52.5	82.6

The distribution ratio of iodine between water and carbon tetrachloride has also been determined by Jakowkin.[1] He calculated his results on the basis of 1000 c.c. of solution and found that the ratio increases from 80.5 in dilute solutions to a value of 89 as the concentration of the iodine is increased. We have found that the value of the ratio for the range of concentrations used is independent of the concentration of the iodine when calculated on either basis. The mean value of the distribution ratio (K = 52.5) is used throughout the work which follows:

Solubility of Iodine in Barium Iodide Solutions

For this purpose solutions of an approximate definite normality were first prepared from the purified salt and air-free conductivity water. Accurately weighed samples of these solutions were taken and the barium precipitated as barium sulphate. The concentrations were then calculated on the basis of mols of barium iodide in 1000 g. water. To make the different dilutions used accurately measured volumes of these solutions were transferred to previously weighed 100 c.c. volumetric flasks and weighed. The solution was then diluted to 100 c.c. at 25° with air-free water and again weighed. From these data it is possible to calculate the concentration at all dilutions on both the weight and volume basis. The solutions were then transferred to dry glass stoppered bottles and an excess of solid iodine was added. The bottles were sealed and rotated in the thermostat for 24 hours, and then allowed to stand in the bath until the finely divided solid iodine had completely settled. Definite samples of the saturated solution were then transferred to accurately tared flaskes containing solutions of potassium iodide, weighed and the iodine determined by titration. From the weight of iodine found, the weight of the sample taken and the concentration of the barium iodide solution we calculated the total concentration of the dissolved iodine.

The results of these determinations are shown in Table II. The molal concentration of the combined iodine was obtained by subtracting the molal solubility of iodine in water from the total amount of the dissolved iodine.

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[1] Jakowkin: Z. physik, Chem., 13, 539 (1894).

TABLE II

The Solubility of Iodine in Barium Iodide Solutions at 25°

$\frac{\text{Mols BaI}_2}{1000\text{ g. H}_2\text{O}}$	$\frac{\text{Mols I}_2}{1000\text{ g. H}_2\text{O}}$	Mols I_2 (combined)	$\frac{\text{Mols I}_2}{\text{Mols BaI}_2}$
0.000000	0.001329	0.000000	——
0.000686	0.002044	0.000715	1.042
0.003120	0.004482	0.003153	1.010
0.006287	0.007574	0.006245	0.993
0.031674	0.032199	0.003087	0.975
0.047716	0.048413	0.04702	0.985
0.080477	(0.079370)	0.07804	(0.969)
0.16497	0.16872	0.16739	1.015
0.34880	0.39500	0.39367	1.129
0.39633	0.45460	0.45327	1.144
0.57189	0.81690	0.81557	1.426
0.87640	1.4674	1.4661	1.673
1.1922	2.2880	2.2867	1.918

Particularly interesting and significant are the data of the last column. It will be observed that the ratio of the mols of combined iodine to the mols of barium iodide decreases to a minimum with increasing concentration of barium iodide and then increases rapidly again as the concentration of the salt is further increased. Furthermore, the value of the ratio approaches 2 at the highest concentration.

The Distribution of Iodine between Carbon Tetrachloride and Barium Iodide Solutions

These experiments were made by taking a series of concentrations of iodine in an approximately given concentration of barium iodide. A sample of barium iodide, accurately weighed to 1 milligram, was transferred to a dry bottle and dissolved in exactly 75 c.c. of air-free water, 25 c.c. of carbon tetrachloride were then added and finally a quantity of solid iodine insufficient to saturate the two layers. The bottle was tightly sealed and rotated in the thermostat for 24 hours. After allowing the bottles to stand until the separation of the two layers was complete definite portions of each layer were carefully run into weighed freshly prepared solutions of potassium iodide, again weighed and the iodine determined by titration. The titration mixtures from the water layer were then acidulated with hydrochloric acid and the barium iodide content determined by precipitation as sulphate. The weight of the water was determined by difference. The concentration of the free uncombined iodine in the water solution was found by dividing the iodine concentration in the carbon tetrachloride by 52.5. From these data we have calculated the molal concentrations of the barium iodide, the free iodine and the combined iodine, and the equilibrium constants. The results of the determinations are tabulated in Table III.

TABLE III

Equilibrium Constants for Barium Iodide Solutions unsaturated with Iodine.

Mols $BaI_2 \cdot$ a	Mols $I_2 \cdot$ b	Free $I_2 \cdot$ $x \cdot 10^4$	$K_1 \cdot 10^4$	$K_2 \cdot 10^7$	$K_3 \cdot 10^4$	$K_4 \cdot 10^7$
0.02308	0.003953	1.359	6.85	2.05	15.06	4.16
0.02299	0.004806	1.654	6.53	2.48	14.73	5.15
0.02295	0.006980	2.635	6.37	4.27	15.37	8.80
0.02289	0.009544	3.865	5.79	5.97	15.45	13.44
0.02312	0.009813	3.935	5.72	6.05	15.39	13.66
0.02292	0.012686	5.603	4.99	8.73	15.57	20.66
0.04600	0.004598	0.799	7.34	1.23	15.48	2.54
0.04582	0.009902	1.849	6.79	2.82	15.41	5.97
0.04647	0.017210	3.406	5.97	5.23	15.35	11.62
0.04627	0.023049	5.038	5.30	7.87	15.62	18.30
0.06867	0.008051	0.954	7.27	1.46	15.51	3.05
0.06834	0.015505	1.957	6.78	3.03	15.51	6.46
0.06910	0.026387	3.629	6.01	5.68	15.64	12.68
0.06893	0.036852	5.559	5.00	8.65	15.55	20.38
0.13828	0.060679	4.240	5.50	6.46	15.24	14.72
0.13830	0.088340	6.993	4.04	10.54	15.08	25.89

The four simplest assumptions that can be made in regard to the equilibrium conditions are these.

1. We may assume with Herz and Kurzer that only one of the iodide ions of barium iodide is capable of combining with iodine, and it combines with one molecule, thus $BaI \cdot I_3 = BaI_2 + I_2$. The equilibrium constant for this is

$$K_1 = \frac{[a-(b-x)]x}{[b-x]}.$$

2. Only one of the iodide ions is capable of combining with iodine and it combines with two mols of iodine. This assumption is represented by the chemical equation: $BaI \cdot I_5 = BaI_2 + 2I_2$. The corresponding constant is

$$K_2 = \frac{[a-\frac{b-x}{2}]x^2}{[\frac{b-x}{2}]}.$$

3. Both iodide ions are equally active in combining with iodine and each combines with one molecule only. This is the assumption of Jakowkin and the chemical equation may be written, $BaI_3 = BaI + I_2$. For this the constant is

$$K_3 = \frac{[2a-(b-x)]x}{[b-x]}.$$

4. Each of the two iodide ions may combine with two molecules of iodine, viz., $BaI_5 = BaI + 2I_2$, where ba corresponds to a half-atom of barium. In this case

$$K_4 = \frac{[2a-\frac{b-x}{2}]}{[\frac{b-x}{2}]}.$$

The values for these four constants have been calculated and are tabulated for the different concentrations in Table III.

Using the solubility data of Table I we have calculated the corresponding values for these constants for solutions saturated with respect to iodine. In these calculations we have assumed the molal solubility of the free iodine (x) to be 0.001329. The results are given in Table IV.

TABLE IV

Equilibrium Constants for Barium Iodide Solutions saturated with Iodine.

Mols BaI_2	Total Mols I_2	$K_1 \cdot 10^4$	$K_2 \cdot 10^7$	$K_3 \cdot 10^4$	$K_4 10^7$
0.000000	0.001329	—	—	—	—
0.000686	0.002044	−0.54	16.27	12.21	50.17
0.003120	0.004482	−0.14	17.30	13.01	52.28
0.006287	0.007574	0.09	17.90	13.78	53.47
0.03167	0.03220	0.35	18.58	13.98	54.82
0.04772	0.04841	0.20	18.18	13.65	54.03
0.08048	0.07937	(0.41	18.76	14.12	55.18)
0.16497	0.16872	−0.19	17.15	12.91	53.16
0.34880	0.39500	−1.52	13.64	10.26	44.94
0.39633	0.45460	−1.66	13.23	9.95	44.12
0.57189	0.81690	−3.95	7.11	5.35	31.88
0.87640	1.4674	−5.35	3.46	2.59	24.57
1.1922	2.8800	−6.36	0.76	0.57	19.17

A survey of the data for solutions of barium iodide unsaturated with respect to iodine (Table III) shows that the values of K_3 are fairly constant for concentrations up to 0.14 M. Evidently then we are safe in assuming that each of the iodide ions of the salt is capable of combining with one molecule of iodine to form the compound $Ba(I_3)_2$. This confirms the work of Jakowkin and of Van Name and Brown. It is clear also that the values of K_1, based on the assumption of Herz and Kurzer, do not even approximately represent the equilibrium conditions. The values of K_1 for each single concentration of barium iodide decrease rapidly with increase in the concentration of the iodine. Equally valueless for these concentrations are the relations indicated by K_2 and K_4.

The data of Table IV show a striking anomaly with regard to the equilibrium conditions. If the equilibria in solutions of barium iodide saturated with iodine are to be explained by the formation of a higher polyiodide, the polyiodide formed is very probably $Ba(I_6)_2$, since the two iodide ions are equally active. Under these conditions we should expect a fair degree of constancy for the values of K_4. The maximum variation in the values of K_4 between the concentration limits 0.003 M and 0.16 M is about 4 percent. On the other hand, the values for K_2 and K_3 for the same range of concentrations are equally good. The values of K_1 (H. and K.) are for the most part negative. It should be observed also that the values for all four equilibrium constants pass through distinct maxima at about 0.03 M BaI_2, and then decrease rapidly with further increase in the concentration of the salt. Further, the concentration giving the maximum value for K is that concentration at which the ratio I_2/BaI_2 is a minimum.

We assume for ternary electrolytes a step-wise dissociation with dilution for moderate concentrations. It is also known that in concentrated solution some ternary electrolytes undergo polymerization and subsequent ionization forming complex ions. Our present ignorance of the nature and extent of the ionization of barium iodide in concentrated solutions renders impossible the calculation of the equilibrium constants for solutions of barium iodide saturated with iodine.

Summary

1. The solubility of iodine in water and in aqueous solutions of barium iodide at 25° has been determined.

2. The distribution ratios of iodine between carbon tetrachloride and water have been redetermined on the basis of mols in 1000 g. of solvent.

3. We have calculated the equilibrium constants based on four different assumptions of possible equilibria for barium iodide solutions both saturated and unsaturated with respect to iodine. For dilute solutions unsaturated with iodine $Ba(I_3)_2$ appears to be the only polyiodide present. For concentrated solutions saturated with iodine the data indicate a mixture of the tri- and penta-iodides.

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BAUDRIMONT AS COLLOID CHEMIST

BY WILDER D. BANCROFT

Last spring Mr. W. A. Bender, chief chemist of the Douglas Pectin Corporation, told me that in the Traité de Chimie, published in 1844-1846, Baudrimont had included a great deal of very good colloid chemistry. After some difficulty I succeeded in securing a copy of the book and I find that Mr. Bender had not exaggerated things in the least.

In the second volume, pp. 842-850, Baudrimont has a chapter on the general characteristics of particulate or non-crystallizable substances. Since particulate is not a word in common usage, I am going to substitute for it the word granular, which means the same thing. "Organic substances occur in a series of stages, rising from the level of inorganic compounds to the structure of organized bodies. In the lowest stage they are like inorganic compounds. Like them they occur and react in definite proportions; they are solid, liquid, or gaseous; their molecules have fixed axes which give them a structure and a definite crystalline form; but they are characterized by their origin and by the nature of the elements which constitute them, typical instances being sugar, alcohol, and the gaseous carbides [hydrocarbons], etc. In the next stage the substances do not have compositions described by the law of definite proportions, they combine in varying proportions, they are formed of particles visible under the microscope and having no definite axes. When left to themselves the particles either remain free and take the form of a liquid, like albumin, or they agglomerate and form tuberculous masses like the gums and the resins. At a still higher stage the particles arrange themselves under the influence of definite forces, forming organic tissues, like the cellular tissues, the muscles, and the nerves. Finally they assume forms and methods of arrangement which vary with the beings to which they give rise.

"The first stage is that which is represented by organic compounds in the strict sense of the word, by the substances described in the first part of the organic chemistry under molecular or definite compounds. The second stage is represented by substances, whose constituent parts, though still subject to the laws of mechanics, adopt nevertheless the form of the constituents of the organic tissues. They are represented by spheroidal particles which are either liquid or seem to be; particles which are formed under the influence of forces peculiar to or inherent in them, if we may use such a phrase. These substances I have called granular and they will be described in the second part of the organic chemistry. At the next higher stage, if exterior forces supervene, the granular constituents agglomerate according to certain laws and form organized beings as has been said. These last two groups of substances belong necessarily under general anatomy and physiology and need not be discussed in a treatise on chemistry, although they have really been studied by chemists. There are now text-books on anatomy and physiology which include all the chemical ideas which are needed.

"The granular substances are formed of spherical or spheroidal particles having diameters varying from two hundredths of a millimeter to about one millimeter. This enormous variation in volume can be observed in some cases with a single kind of particle, starch, for instance. When the particles are brought in contact with certain liquids, they either take up the liquids and swell considerably or they yield a part of the liquid they contain to the surrounding fluid and shrink. The first phenomenon occurs strikingly with starch grains in boiling water or in hot acidulated water; with histose, the cellular tissue of animals, in presence of boiling water. The second phenomenon can be observed by putting grains, such as gum arabic, into alcohol after they have swelled in water.

"When the particles are swollen very much and are held in suspension in a liquid, they seem to be dissolved but they are not. Albumin and gum arabic are usually called soluble in water; but they are not really soluble and only seem to be, their special structure permitting the particles to slide one upon another and thus duplicate in mass the properties of a liquid, while they also give this seeming liquid a special viscosity because of the mutual adhesion.

"If the liquid in contact with the grains has some chemical substance in solution, this substance may penetrate the grains and be held there by a variable force, of a nature similar to that which causes solution and capillary phenomena. Very soluble salts may therefore be retained by the particles even after a number of washings. It is for this reason that it is almost impossible to remove potassium acetate which has been adsorbed by protein. The granular substance may even protect the adsorbed substance so completely that the latter will resist a chemical attack which would ordinarily dissolve it. Fibrin will retain phosphates so that only with extreme difficulty can hydric salts [acids] dissolve them readily under ordinary conditions. There seems to be a sort of adhesion which holds together the particles and the substance fixed by them.

"The substances held in a state of pseudo-combination by the granules modify the properties of these latter remarkably. Since the granular substances are generally not soluble and would lose all their characteristics properties if they were soluble, the adsorption may prevent them from expanding [dispersing] sufficiently in a liquid to appear soluble and we therefore say that they have become insoluble. Substances, which make the granules contract, may precipitate them.

"Among the modifications of the granules when in pseudo-combination, two are very remarkable. In one the particles become visible and may be said to be solidified; but they remain isolated. This occurs with barium hydroxide and albumin. In the other case the particles contract and agglomerate to form a clot. In other words, coagulation occurs. We get this when alcohol, chloromercuric acid, or the mineral acids, with the exception of phosphoric acid, react with albumin. To what is due the repulsion or adhesion? What gives rise to these differences? These are questions with which the future will have to occupy itself and which will perhaps clear up what happens in the organs of living beings when the constituents which form them are fixed.

"The union just described is very different from chemical combination; it does not affect the molecules and is not according to definite proportions. The amounts which combine are proportional to the time [?] and to the temperature. This accounts readily for the fact that chemists have believed in an increasing saturation capacity which nevertheless gave definite compounds. Instances of this are the facts observed by M. Frémy in his work on pectin and by M. Mulder in his work on fibrin. The latter chemist claims that fibrin obtained from blood from the jugular vein of a cow gave a sesquifibrate of silver, while fibrin prepared from arterial blood obtained by cutting the carotid artery of the same animal gave quadrifibrates. All the alleged, definite compounds of albumin, fibrin, pectin, pectic acid, etc., are indefinite compounds in varying proportions, which may nevertheless have a definite limit; but this limit is comparable to the limiting amount of water which a sponge can take up.

"There is one conclusive proof of the views which have just been put forward. So long as a granular substance is not destroyed, it keeps its particulate state no matter what combination is formed. I have treated pectin with a number of reagents, obtaining apparent compounds and double decompositions. In every case the new compounds were particulate and when one regenerated the pectin from a series of compounds, it had its original properties and its granular form."

"The extraction and purification of granular substances is a very special problem. They cannot be dissolved and allowed to crystallize; they cannot be distilled or sublimed. If one were to dissolve them, to make them form real compounds or to change their physical state, they would lose entirely the structure which characterizes them and they would not regain it, if we assume that this structure us usually the result of organic functions. We must therefore purify granular substances by a series of treatments which will not alter them but which will destroy the impurities which are present. We obtain cellulose, protein, and casein for instance, by treating them successively with acids, alkalies, ether, alcohol.

"The occurrence of inorganic compounds in the granular substances interferes very much with the accuracy of the analytical results that one gets. We usually assume that the weight of the organic portion is equal to the difference between the total weight of the substance and the weight of the ash obtained by combustion. The ashes, however, are not necessarily in the same state of combination as in the original substance. The iron may be ferric and not be ferrous; there may be carbonates instead of salts of organic acids. If such analyses are to be significant, it is essential to know the form in which the inorganic bases occur in the organic substance, to make an accurate analysis of the ash, to calculate the form in which the bases were, and to correct the experimental data in accordance with this.

"As has already been said the granular masses behave like liquids, jellies, or amorphous and vitreous substances. Liquids containing particles in a state of pseudo-solution [colloidal solution] are always viscous. If the viscosity increases, that is if the granules become more adherent, they unite and form a jelly, like starch, paste, the mucilaginous gums, pectin, gelatin, and chondrin. In the solid state they form lumpy masses like the gums, the starches, the fats, and cellular tissue. The property of forming a viscous liquid or of setting to a jelly is so limited to the granular substances that I have not found a single substance with this property which did not have a particular structure. Typical cases are the glairy substance in mineral waters, the mucus of viscous fermentation, the pseudo-solutions of gums, albumin, animal jellies, etc. All these owe their properties to the granular nature of their constituents. I even dare to add that all substances, like the gums, which are amorphous and vitreous are particulate and that so are potassium silicate jelly, viscous sulphur, the different forms of glass, the hydrated silica obtained by M. Ebelmen, hyalite, the resins, agate, etc.

"The particles are formed by the dispersion of a pre-existent liquid or by the formation of one liquid in another liquid which cannot dissolve it. A small amount of liquid left to itself in the mass of another liquid will tend to become spherical and will become spheroidal under the influence of gravity or other forces. One sees this if one drops mercury on a table or disperses oil in mucilage. One must therefore assume that all the organic granules have passed through the liquid stage. . . .

"The knowledge of the granular state of organized bodies clears up many facts hitherto inexplicable and leads to many applications. It explains the formation of organic substances, a number of physiological phenomena, the part played by mineral fertilizers, the constitution of the skeleton, the dyeing of textiles, the tanning of skins, etc.

"The opinion has already been expressed that organic tissues were formed of granules[1] and this view was rejected for many reasons, among others that some of the infusoria have organs smaller than the smallest granules and that consequently all animal tissues cannot be particulate. That may be true but they have credited the infusoria with many organs which they do not possess and I am also prepared to state that many of the infusoria are formed entirely of globules. Anyhow, this does not invalidate anything which has been said because we have been talking about beings higher in the organic scale, for which the proof is positive and not to be overthrown by any objections.

"We may therefore consider all the statements in the preceding paragraphs as absolutely accurate. They are true for all the substances which are to be discussed in the remaining pages of this volume. It is in consequence of unpublished microscopic observations and tests, covering a period of nearly twenty years, that I am able to gather together and to correlate all these results, which create a new branch of chemistry."

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[1] Here Baudrimont is apparently using the word in the sense of cells.

Baudrimont considers that the particles of gelatine, for instance, swell in water and thereby become invisible. He does not seem to have considered the possibility of their being dispersed into smaller particles and consequently we cannot credit him with a knowledge of peptization. Baudrimont did not know that the soaps form true solutions in alcohol and colloidal ones in water and he believed in colloidal substances rather than colloidal states; but so did Graham and, for that matter, so did the rest of us up to relatively few years ago.

On the other hand Baudrimont was perfectly clear that the second substance in a colloidal solution is not in solution but only appears to be. He knew about adsorption and, though he never heard of an adsorption isotherm, he knew that adsorption may soon reach a practical limit with increasing concentration. He knew that suspended particles may swell without forming definite hydrates and he knew that jellies are formed by the partial agglutination of the suspended particles. He knew that adsorption may change the apparent physical and chemical properties of the adsorbed substance and that the adsorbed substance may coagulate and precipitate the adsorbing colloid. He knew that most of the alleged compounds with colloids did not exist. In short, Baudrimont knew a great deal more about colloid chemistry ninety years ago than some distinguished scientific men do now.

One or two special quotations will emphasize Baudrimont's point of view. "Gum arabic appears to be soluble in water but does not dissolve in it. The particles separate, imbibe liquid, become soft and flexible, and therefore share the dynamic conditions of equilibrium of the water which holds them in suspension. The viscosity of the liquid is increased considerably by the adhesion of the particles of gum arabic. Alcohol cannot break apart the particles of gum arabic and hold them in suspension as water does. When one adds alcohol to the seeming solution of gum arabic, it causes them to contract and precipitate," p. 853. "Casein occurs in milk and appears so completely dissolved that it is impossible to see it. The only particles that one sees directly are those of the butter fat. Nevertheless suitable reagents cause the casein to contract and the particles then become visible. For a long time casein was considered to be soluble in water; but, quite independently of my observations. M. Rochleder has shown that water does not dissolve any casein when the latter is pure," p. 879. Casein is not considered by Baudrimont to form definite compounds either with acids, alkalies, or salts.

"Albumin occurs in the form of absolutely invisible particles when one examines it without any additions; but when a suitable reagent is added the particles become readily visible and easily recognized. Barium hydroxide solution is the best reagent for this purpose. When made visible in this way, the particles of blood albumin are much smaller than the red blood corpuscles and are only 0.005 mm in diameter. The particles of egg albumin from two lots of hen's eggs were 0.006 mm in diameter," p. 884. "Gelatine is particulate, solid, transparent, colorless, denser than water, hard like horn, fragile, and with a conchoidal fracture when it is very dry, while it is flexible, very elastic, and very tough when it is a bit damp. . . . Put in contact with water at room temperature, it swells, losing its limpidity and solidity. If, after it is permeated by water [not hydrated], it is heated to 50° or 60°, the gelatine appears to dissolve completely; but it is really only held in suspension, as can be shown by microscopical examination after treatment with suitable reagents, and as is also proved by the gelatinous state to which it returns on cooling," p. 896.

In the first volume Baudrimont points out, p. 198, that probably all solids show what we now call selective adsorption, especially when they are porous with fine pores. He considers, p. 81, that dyes are taken out of solution by the textile fibers and made apparently insoluble without forming any definite compounds. The phenomenon is analogous to the decolorizing by charcoal, which everybody knows does not involve the formation of definite chemical compounds. Even the taking up of cochineal by cotton mordanted with alumina is thought to be a case of adsorption, p. 198.

Although very clear on the subject of dyeing, the question of mordants was rather too much for Baudrimont.[1] "Alum alone does not cause any precipitate in a solution of carmine; but it has the remarkable property of fixing the carmine on textiles. A textile can be immersed in a solution of carmine without being dyed in the least. It only soaks up the dye which can be removed completely by a few washings. Alum does not precipitate carmine and yet, if the textile has previously been impregnated with an alum solution, the coloring matter becomes fixed on the cloth and cannot be removed ay any number of washings. This is a general phenomenon. Infusions or solutions of coloring matters can only be fixed upon textile by metallic salts. Such salts are called mordants."

What Baudrimont has overlooked is that impregnating cloth with a solution of alum precipitates in the fibers either alumina or a basic salt. Either of these will take carmine out of solution in the absence of the cloth. One must not hold this minor slip up against him in view of what he goes on to say about dyeing. "Under the conditions just mentioned, the cloth, or the threads from which it is made, function by some sort of capillary action, for they are not destroyed. The dye is only fixed on their particles forming a special type of compounds in which the molecules are not changed. Such compounds have been called particulate [indefinite or adsorption compounds]. For any coloring matter, inorganic or organic, to unite with a textile and dye it in a durable manner, the dye must be dissolved in a medium so that it can impregnate the textile and be made insoluble by it. This is the fundamental principle in all dyeing. A few instances will suffice. Orpiment [arsenious sulphide] is used as a dye by dissolving it in ammonia, dipping the cloth in the bath, and letting the ammonia evaporate, when the cloth will be found to be dyed. One can produce double decomposition in the fabric, as in dyeing yellow, by impregnating the cloth in a solution of a lead salt and then dipping it in a solution of potassium chromate which reacts with the lead salt to form lead chromate. Dyeing with Prussian blue is done in a similar way. Indigo white, dissolved

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[1] Traité de Chimie, 2, 24, 756 (1846).

in water, will penetrate the threads and becomes insoluble and blue on contact with the oxygen of the air. As has been mentioned, dyes may be fixed on the fabric by mordants. The sole function of mordants is not to fix dyes. Different mordants may give different colors and a single immersion in a madder bath may dye the cloth five or six different colors according to the mordants printed on the cloth in advance."

Baudrimont[1] might have discovered the mass law years before Guldberg and Waage if he had done a few experiments instead of merely talking about them. He calls attention to the extraordinary fact that iron oxide can be reduced to metallic iron by hydrogen with the formation of water and that iron can be oxidized to an oxide by steam with the formation of hydrogen. He points out that these apparently contradictory results are due to the effect of mass. "It is the preponderance of the water vapor over the hydrogen in the one case which causes the iron to be oxidized and keeps the oxide from being reduced. It is the preponderance of hydrogen over water vapor in the other case which causes the oxide of iron to be reduced and keeps the metal thus produced from being oxidized. Perhaps it would be possible to make a mixture of hydrogen and water vapor which would be without action either on iron or iron oxide. If so, the ratio of the two quantities of these substances would give that of their chemical masses. An experiment of this sort would be easy to do with carbon monoxide and carbon dioxide."

The experiments apparently never were made; but I hope that these quotations will show that Baudrimont was not a man to be forgotten profitably even though his work along these lines had absolutely no effect so far as we now know. It is a discouraging point of view; but apparently a good idea at the wrong time or by the wrong man, which is perhaps the same thing, is apparently as much wasted as though it had never occurred. One can console oneself however by assuming that if it were not for these preliminary and apparently futile efforts, the right time and the right man would never come. Emerson did not love the Irishman but he thought up a use even for him.

Cornell University.

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[1] Traité de Chimie, 1, 183 (1844).

THE DETERMINATION OF SOFTENING TEMPERATURES BY THE FLUIDITY METHOD

BY EUGENE C. BINGHAM

The determination of the melting-point of a soft solid which melts to a very viscous liquid has long presented a difficult problem, so that many substances are said to have a "softening temperature" rather than a melting-point and it is not clearly understood whether a definite transition temperature really exists. If waxes, resins, pitches, *et cet.* do show a sharp transition temperature from the viscous to the plastic regime and *vice versa*, the fact may have an important bearing on the control of colloidal materials, as previously pointed out[1]. Some of the plastics used in dentistry seemed to afford an opportunity for studying the possibility of using the viscometer or plastometer in attacking this problem.

In making artificial dentures, it is necessary to obtain a very accurate impression of the inside of the patient's mouth in order to obtain a well-fitting plate. For this purpose Plaster of Paris was formerly used but plastics have recently been devised which will become soft enough to mold very readily at temperatures which can be tolerated in the mouth; yet at the temperature of the body the materials are rigid enough to hold their shape permanently. These plastics are made from varnish resins mixed with stearic acid, talc and coloring matter.

Two compounds designated T and E, obtained from the S. S. White Dental Mfg. Company were studied. The resin content in both was the same. Compound T contained 40% stearic acid by weight. In compound E, 6% of stearic acid was replaced with mineral oil of viscosity 187 Saybolt seconds at 50°C.

To compound T, 44.5% talc by weight or 22.0% by volume was added, the mixture becoming TB.

To compound E, 50% talc by weight or 26% by volume was added orming mixture ER.

The coloring matter made up an inappreciable percentage of the whole. The instrument used was the plastometer already described in Bulletin 278 of the U. S. Bureau of Standards. A capillary was used having a length of 7.09 cm. and a radius of 0.0504 cm.

The data obtained are given in Table I and plotted in Figure I. If the materials used are plastic solids, the fluidity should continually decrease as the shearing stress is lowered. In none of the materials was there any evidence of this, hence we must assume that the materials have such a small yield value, if any at all, that they behave as viscous liquids. In certain cases the volume of flow was very small (0.04 g.) hence the percentage of error is much higher

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[1] Bingham: Ind. Eng. Chem. 14, 1014 (1922).

than need be with a more favorable disposition of apparatus. In these preliminary experiments a long and narrow capillary was preferred.

The fluidity of each material decreases in a *linear* manner as the temperature is lowered so that each material has a definite transition temperature from the plastic to the viscous condition. Moreover, this transition temperature is not affected by the addition of solid material like talc. The substitution of 6% of oil for an equal per cent of stearic acid increases the fluidity of the compound and lowers the transition temperature from 45.2°C to 42.4°C. The addition of talc to either wax base lowers the fluidity rapidly, but in a peculiar manner. Thus a given percentage of talc lowers the fluidity a constant percentage of its value, irrespective of what the fluidity may be, due to the changes in temperature. This is quite similar to the behavior of suspensions in water studied by Bingham and Durham. From a practical point of view, this lowering of the temperature coefficient of fluidity has the effect of extending the temperature range over which the material is workable. It may be noted that both materials containing talc are made up to have practically the same fluidity at 55°C. Since the base T has a much lower fluidity (21.9) than the base E (36.0), the percentage of talc necessary to be added to the former is only 44.4 per cent whereas the latter required 50 per cent.

The material ER has the advantage over TB in that it would have a considerably greater range of temperature in actual use, during which the material could be molded, but it would presumably have the disadvantage that at the temperature of the body (37°C) the material would be so near the transition temperature that considerable care would be necessary in handling. On the other hand, the material TB would be expected to have a higher yield value, but it should be used at the highest practicable temperature.

Earlier work would lead one to suppose that the talc would lower the fluidity in a linear manner and we would expect that the same percentage of talc would be necessary with either base, in order to obtain zero fluidity. Assuming a specific gravity for talc of 2.75 the mixture TB contains 22 per cent. by volume and the composition having zero fluidity would contain 26.7 per cent. The mixture ER contains 26 per cent. of talc by volume and the mixture of zero fluidity would contain 29.3 per cent. by volume. These figures are not quite identical as they should be. This may be explained by the difficulty of removing the air which is incorportated with the talc in the material. More of this remains in that mixture having the higher percentage of talc and the air naturally adds to the fluidity of the mixture.

A most interesting question is in regard to the nature of the transition point. It is obviously not a melting-point because when pure liquids are cooled the fluidity reaches the zero value asymptotically unless crystallization intervenes, in which case there is a sudden drop in the fluidity. In these waxes there is no sudden drop and yet the zero value is not approached asymtotically. When the materials have zero fluidity, they must possess a structure which obstructs the flow. If the structure does not develop suddenly it must develop gradually as the material is cooled. Moreover the structure must be due to the stearic acid since that is the constituent which affects the temperature of zero

TABLE I

THE FLUIDITY OF DENTAL WAXES

Temperature	Pressure gm. per cm²	Efflux gm./sec × 10⁶	Fluidity × 10⁵ Observed	Avg.	Calc.
Compound "T"					
55°	317	23.5	22.0	21.9	21.9
55	647	49.7	22.8		
55	1245	93.3	22.3		
55	1658	114.3	20.6		
50	1658	57.1	10.1	10.2	10.7
50	1245	44.0	10.4		
50	647	22.3	10.1		
47.5	1658	33.0	5.9		5.1
46	1658	3.8	0.7		1.8
$\phi = (T - 45.2)\, 2.23 \times 10^{-5}$					
Compound "TB"					
55	1656	30.3	3.9	3.9	3.8
55	1968	36.0	3.9		
50	1656	14.4	1.9		1.9
$\phi = (T - 45.2)\, 0.385 \times 10^{-5}$					
Compound "E"					
55	827	103	37.5	36.0	36.2
55	1245	141.	34.0		
55	1658	208.	37.7		
55	1245	144.	34.7		
52	1245	116.2	27.8		27.6
50	1245	89.9	21.3		21.7
48	1245	66.8	15.7		16.1
45	1658	42.6	7.4		7.5
$\phi = (T - 42.4)\, 2.87 \times 10^{-5}$					
Compound "ER"					
55	1245	25.6	4.2	4.0	4.0
55	1658	31.2	3.1		
55	1968	44.3	4.6		
50	1968	21.0	2.2		2.4
45	1968	8.2	0.8		0.8
$\phi = (T - 42.4)\, 0.317 \times 10^{-5}$					

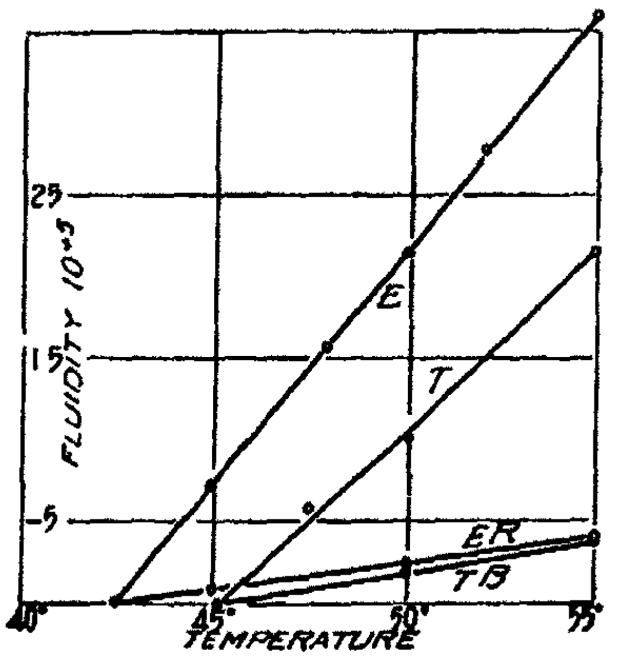

FIG. 1

Fluidity-temperature relationships for:
Exact impression compound = E
Do. with talc and color (red) = ER
Tray impression compound = T
Do. with talc and color (black) = TB

fluidity, at the concentrations studied. The conclusion therefore seems to be necessary that a part at least of the stearic acid is present not as a true solution in the resinous substance but in colloidal solution. As the temperature is lowered the particles of stearic acid increase either in number, or in size, or both, until they come within range of each other and flow is interferred with. This is then the transition temperature.

Below the transition temperature the material is still soft and therefore plastic. It is hoped to measure the plasticity and elasticity later. From the work which has been done with suspensions it might be expected that these materials would exhibit pseudo-plastic flow with small though measurable yield values well above the transition point. But if this eccentricity of flow is due to seepage it is not surprising that it is absent from such extraordinarily viscous material as that with which we are here dealing.

In the table the pressures are corrected for hydrostatic head. The efflux from the capillary is given in grams per sec. $\times 10^6$ in column 3. The fluidity in absolute units $\times 10^5$ is given in the fourth column, while in the last column are given the fluidities calculated by linear formula, given in the table.

Since for these experiments the radius of the capillary was determined merely by the weight of a mercury thread, the values of the fluidity are not claimed to be exact, and for the present there is no need that they should be. However it is hoped later to test these conclusions with other capillaries. Murray has proved that for absolute measurements of flow, capillaries must be measured with great care.

Another source of embarrassment in measurements of the flow of very viscous materials should be mentioned. They often contain solid particles, filter shreds *et cet.* which are accidentally present but which may greatly change the character of the flow through capillary tubes if not removed. The material studied in this paper contains particles which do not become disintegrated as the temperature is raised. Similarly nitrocellulose is not completely soluble in acetone or other solvents, a residue remaining which partly settles out on standing. Also rubber is not completely soluble in benzene. The insoluble part will not pass through the capillary of the viscometer but it is very difficult to separate it by filtration.

Conclusions

1. Varnish gums mixed with stearic acid, with or without mineral oil, show a sharp transition temperature between the viscous and plastic conditions.

2. The fluidity-temperature curves of these materials are linear over the range studied.

3. The addition of finely-powdered solid matter (talc) to these mixtures greatly lowers the temperature coefficient of fluidity without changing the transition temperature between the viscous and plastic condition.

4. The transition temperature can be readily lowered by substituting mineral oil for part of the stearic acid.

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Easton, Pa.
Sept. 17, 1923.

THE ADSORPTION OF BINARY MIXTURES BY ANIMAL CHARCOAL AND A COMPARATIVE STUDY OF THE ADSORPTIVE POWER OF DIFFERENT VARIETIES OF CHARCOAL

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The phenomenon of adsorption is of very great importance both from theoretical and practical points of view. It plays a great part in the domain of the organic world. Some of the most important industries are based upon this principle. On the theoretical side it presents various related phenomena for investigation but up till now very little work has been done on this interesting subject which undoubtedly deserves a greater amount of attention than has been hitherto shown to it and up till very recently the subject had been a neglected one. On consulting the literature, the latest work on the subject was by Nikili Schilaw and Ledi Lepin. Their work throws a flood of light on the nature of phenomenon itself and opens up many new lines for further investigations. One of the subjects studied by them is that of adsorption of mixtures, but, as they have restricted their work in detail to a few substances, it was considered advisible to carry on further investigation on the subject and to see if it would be possible to find out whether the adsorption of mixtures follows any definite rule whether the results could be expressed by any stoichiometric relations.

1. Purified charcoal from Messrs Baker and Co., London was used. It did not require any further heating for it did not contain any tarry matter; but it was subjected to the following operations previous to its use in experiments. It was crushed very fine and put in a solution of HCl and HNO_3 for five days after which it was washed free of acid with boiling distilled water. It was then dried and powdered, passed through a sieve to secure uniformity of the size of particles, and then stored in corked bottles. The electrolytes used were the chlorides of sodium, potassium, magnesium, lithum, barium and calcium; and KOH, NaOH, HCl, HNO_3, $(COOH_2)$, Na_2CO_3.

Experiments were performed in small flasks which contained a known weight of charcoal (2 grams) in which 25 cc of a solution of known concentration were introduced and left for 20 minutes. During this time the flasks were occasionally shaken. The amount adsorbed was determined by finding out the concentration of a solution after it was acted on by charcoal, the initial concentration of that solution being known.

A number of preliminary experiments were performed to check the adsorbing property of each new portion of charcoal that was used. Temperature and dilution effects were also observed. It was found that the temperature effect is very small and is positive i.e. a very small increase of adsorption takes place with a great increase in temperature. The effect of the change of concentration is remarkable. At low concentrations the relative amount of adsorption is greater than at high concentrations.

Preliminary Experiments

(a) *Control experiments.*

As a large number of experiments were performed with animal charcoal the adsorbent property of each new portion that was prepared was controlled by a few experiments. They are shown in Table I. The solutions with their concentration are given in the first end column. In these and the following experiments C_1 and C_2 indicate the original and final concentrations, A the adsorbed amount and $(A \times 100)/C_1$ is the ratio of the adsorbed amount to the original concentration of the solutions.

TABLE I

Solutions and conc.		C_1	C_2	A	$(A\times 100)/C_1$
HCl N/40	(1)	25.0	16.50	8.50	34.0
" "	(2)	25.0	16.40	8.60	34.40
" "	(3)	25.0	16.30	8.70	34.80
" "	(4)	25.0	16.45	8.55	34.20
NaOH N/40	(1)	25.0	14.00	11.00	44.00
" "	(2)	25.0	13.95	11.05	44.20
" "	(3)	25.0	14.05	10.95	43.20
" "	(4)	25.0	14.10	10.90	43.60

It can be seen from the above table that the adsorbed amounts in each experiment in both the cases are fairly constant. This shows that the charcoal must have undergone a similar treatment during the purification. Adsorption values obtained with each portion of charcoal can be compared with a fair degree of accuracy.

(b) *Temperature effect.*

Before proceeding with the main work a large number of experiments were performed in order to find out the effect of temperature and concentration upon adsorption. Experiments were performed the same way as already mentioned with the same weight of charcoal unless otherwise stated and with the same time schedule. The solutions were maintained at constant temperature in a thermostat. Experiments were performed at 25°, 50°, 75°, and at the temperature of boiling water which was 99.8° and they are given in Table II. C_1, C_2, A, and $(A\times 100)/C_1$ have the same meaning as before. The solutions worked with and their concentrations are shown in the front column.

TABLE II

Oxalic acid	C_1	C_2	A	$(A\times 100)/C_1$
		Temp. 25°		
2N	25.00	22.3	2.70	10.80
N	25.00	19.15	5.85	23.40
N/2	25.00	17.00	8.00	32.00
N/4	25.00	16.25	8.75	35.00
N/8	25.00	16.00	9.00	36.00
		Temp. 50°		
2N	25.00	21.59	3.41	13.64
N	25.00	18.625	6.375	25.50
N/2	25.00	16.25	8.75	35.00
N/4	25.00	15.75	9.25	37.00
N/8	25.00	15.00	10.00	40.00
		Temp. 75°		
2N	25.00	21.575	3.425	13.70
N	25.00	18.25	6.75	27.00
N/2	25.00	16.35	8.65	34.60
N/4	25.00	15.70	8.30	37.70
N/8	25.00	15.00	10.00	40.80
		Temp. 99.8°		
2N	25.00	20.62	4.38	17.52
N	25.00	17.78	7.22	28.88
N/2	25.00	16.30	8.70	34.80
N/4	25.00	15.50	9.50	38.00
N/8	25.00	14.50	10.50	42.00
KOH	C_1	C_2	A	$(A\times 100)/C_1$
		Temp. 25°		
2N	25.00	21.20	3.80	14.20
N	25.00	20.75	4.25	17.00
N/2	25.00	19.50	5.50	22.00
N/4	25.00	17.825	7.175	28.50
N/8	25.00	9.25	15.75	63.00
		Temp. 50°		
2N	25.00	20.225	4.775	19.10
N	25.00	20.02	4.98	19.92
N/2	25.00	18.75	6.26	24.00
N/4	25.00	17.77	7.23	28.92
N/8	25.00	8.25	16.75	67.00
		Temp. 75°		
2N	25.00	20.04	4.96	19.84
N	25.00	18.63	6.36	25.44
N/2	25.00	15.98	9.02	36.08
N/4	25.00	15.35	9.65	38.60
N/8	25.00	8.75	16.25	65.10
		Temp. 99.8°		
2N	25.00	20.10	4.90	19.60
N	25.00	18.40	6.60	26.40
N/2	25.00	15.33	9.67	38.68
N/4	25.00	15.235	9.765	39.06
N/8	25.00	8.64	16.56	66.25

These results are for four grams of charcoal

On summarising the results obtained above at different temperatures we get:—

Oxalic acid	25°	50°	75°	99.8°
2N	10.80	13.64	13.70	17.52
N	23.40	25.50	27.00	28.88
N/2	32.00	35.00	34.60	34.80
N/4	35.00	37.70	37.70	38.00
N/8	36.00	40.00	40.80	42.00
KOH	25°	50°	75°	99.8°
2N	14.20	19.10	19.84	19.60
N	17.00	19.92	25.44	26.40
N/2	22.00	25.00	36.08	38.68
N/4	28.50	28.92	38.60	39.06
N/8	63.00	67.00	65.10	66.25

Interpretation of Results

It is seen from the column under $(A\times 100)/C_1$ that this ratio for a substance at one concentration and with different temperature does not vary very much on the whole and so the effect of temperature on the adsorbed amount is very small. If experiments are performed at room temperature without a thermostat, no serious error is involved. These results are confirmed by the results of Schmidt and Freundlich. Similar conclusions have been arrived at by Walker and Appleyard.

The increase of adsorption with increase in temperature, though very small, has been traced to the removal of air from hollow spaces within the body of charcoal and to the decrease in the solubility of air at high temperatures.

(c) *Concentration effect.*

For experimental work see Table II.

Interpretation of results. It is also seen from the above tables that a substance is adsorbed relatively more at low concentrations than at high concentrations. Comparison of numbers for one substance under $(A\times 100)/C_1$ at one temperature with increasing dilution shows that this number increases but it may be observed that the absolute amount of adsorbed substance is more at high concentrations than at low concentrations. In other words the adsorbed amount is a direct function of the concentration.

The relative increase of the adsorption with dilution is not to be ascribed to the increase in dissociation of an electrolyte in solution for non-dissociation of an electrolyte in solution for non-dissociating substances or non-electrolytes also behaved similarly. This may be due to the greater mobility of molecules in solution with decrease in concentration and hence to the greater number of contacts to which a charcoal particle is subjected.

Actual Experiments

Adsorption of single substances.

Before the effect of a foreign substance on the adsorption of another substance can be found out, the adsorption of the former when alone should be tried first and so the following experiments have been devoted to the adsorption of pure substances. The method of these experiments is the same as already described except that they were performed at room temperature without a thermostat. Weight of charcoal used in each experiment was two grams and the time was twenty minutes.

TABLE III

Solutions and conc.		C_1	C_2	A	$(A\times 100)/C_1$
HCl	N/10	25.00	18.05	18.50	27.50
”	N/20	25.00	17.50	7.50	30.00
”	N/40	25.00	16.50	8.50	34.00
H_2SO_4	N/10	25.00	16.38	8.62	34.50
”	N/20	25.00	15.25	9.75	39.00
”	N/40	25.00	13.50	11.50	46.00
HNO_3	N/10	25.00	16.75	8.25	33.00
”	N/20	25.00	15.25	9.75	39.00
”	N/40	25.00	12.45	12.55	50.2
$(COOH)_2$	N/10	25.00	9.85	15.15	60.6
”	N/20	25.00	7.95	17.05	68.2
”	N/40	25.00	5.0	20.0	80.0
Na_2CO_3	N/10	25.00	18.25	6.75	27.00
”	N/20	25.00	16.75	8.25	33.00
”	N/40	25.00	15.50	9.5	38.0
NaOH	N/10	25.00	15.50	9.50	38.00
”	N/20	25.00	14.50	10.50	42.00
”	N/40	25.00	14.10	10.90	43.60
KOH	N/10	25.00	13.375	11.625	46.50
”	N/20	25.00	13.00	12.00	48.00
”	N/40	25.00	11.00	14.00	56.00
KCl	N/5	25.00	23.43	1.57	6.28
”	N/20	25.00	23.19	1.81	7.24
”	N/40	25.00	22.94	2.06	8.24
NaCl	N/2	25.00	23.575	1.425	5.70
”	N/5	25.00	23.50	1.50	6.00
”	N/20	25.00	23.50	1.50	6.00
”	N/40	25.00	23.40	1.60	6.40
$MgCl_2$	N/5	25.00	24.30	0.70	2.80
”	N/10	25.00	24.18	0.82	3.20
”	N/20	25.00	23.875	1.125	4.50
”	N/40	25.00	23.50	1.50	6.00
LiCl	N/5	25.00	24.125	0.875	3.30
”	N/10	25.00	24.06	0.94	3.76
”	N/20	25.00	23.875	1.125	4.50
”	N/40	25.00	23.75	1.25	5.00
$SrCl_2$	N/5	25.00	23.35	1.65	6.60
”	N/20	25.00	23.10	1.90	7.60
”	N/40	25.00	23.05	1.95	7.80
$CaCl_2$	N/5	25.00	23.875	1.125	4.50
”	N/20	25.00	23.50	1.50	6.00
”	N/40	25.00	22.75	2.25	9.00

Interpretation of Results

The effect of dilution in the above results is remarkable. The relative adsorption increases with fall in concentration. With some exceptions the sequence of the atomic weight has a noticeable effect on the adsorption.

Adsorption of mixtures.

Mixtures of the above electrolytes have been made use of in the determination of the effect of one electrolyte on another. The method of experiments is similar to that in the previous cases but with some modifications. This will be clear from the following example:—

25cc of a mixture of N/20 HCl and N/20 LiCl were prepared by mixing 12.5cc of N/10 HCl and 12.5cc of N/10 LiCl. Solutions at other concentrations were prepared in like manner.

The representation of results is a little more complicated. Under C_2 there are two columns, (a) represents end concentrations when a substance before which a value in the tables is put, is acted upon by charcoal when alone; i.e. in a pure condition, (b) when mixed with other substances. The meaning of two columns under each of the two heads (A) and $(A\times 100)/C_1$ is to be interpreted similarly. D represents the difference between the two columns under $(A\times 100)/C_1$. It shows the direction and amount of change which the presence of a foreign substance has effected on the adsorption of another substance. The method of work is quite the same as in former cases. Estimations of the solutions were made when they were neutral.

TABLE IV

KCl. $C_1 =$ 25.00cc,

Solutions and Conc.	C_2		A		$(A\times 100)/C_1$		D
	(a) Sept.	(b) Toget.	(a) Sept.	(b) Toget.	(a) Sept.	(b) Together	
N/20KCl	23.19	23.00	1.81	2.00	7.24	8.00	+0.76
+N/20 HCl	17.50	18.25	7.50	6.75	30.00	27.00	−3.00
N/20KCl	23.19	22.88	1.81	2.12	7.24	8.48	+1.24
+N/40HCl	16.50	17.00	8.50	8.00	42.00	42.00	−2.00
N/20 KCl	23.19	24.25	1.81	0.75	7.24	3.00	−4.24
+N/20H_2SO_4	15.25	17.50	9.75	7.50	39.00	30.00	−9.00
N/20 KCl	23.19	23.25	1.81	1.75	7.24	7.00	−0.24
+N/40H_2SO_4	13.50	14.50	11.50	10.50	46.00	42.00	−0.20
N/20 KCl	23.19	23.60	1.81	1.40	7.24	5.60	−1.64
+N/20HNO_3	15.25	14.12	9.75	10.88	39.00	43.52	+4.52
N/20 KCl	23.19	23.60	1.81	1.40	7.24	5.60	−1.64
+N/40 HNO_3	12.45	11.50	12.55	11.50	10.20	46.00	−4.20
N/20 KCl	23.19	22.50	1.81	2.75	7.24	11.00	+3.76
+N/20$(COOH)_2$	7.95	8.61	17.05	16.39	68.20	65.56	−2.54
N/20 KCl	23.19	22.00	1.81	3.00	7.24	12.00	+4.76
+N/40$(COOH)_2$	5.00	8.25	20.00	16.75	80.00	67.00	−13.00
N/20 KCl	23.19	22.75	1.81	2.25	7.24	9.00	+1.76
+N/20(KOH)	13.00	14.75	12.00	10.25	48.00	41.00	−7.00
N/20 KCl	23.19	21.75	1.81	3.25	7.24	12.90	+5.66
+N/40 KOH	11.00	13.25	14.00	11.75	54.00	47.00	−7.00
N/20 KCl	23.19	23.25	1.81	1.75	7.24	7.00	−0.24
+N/20Na_2CO_3	16.75	18.38	8.25	6.62	33.00	26.48	−6.52
N/20 KCl	23.19	22.75	1.81	2.25	7.24	9.00	−1.76
+N/40 Na_2CO_3	15.50	17.25	9.50	7.75	38.00	31.00	−7.00
N/20 KCl	23.19	22.00	1.81	3.00	7.24	12.00	+4.76
+N/20 NaOH	14.5	19.21	10.50	6.79	42.00	23.06	−8.94
N/20 KCl,	23.19	21.00	1.81	4.00	7.24	16.00	+8.76
+N/40 NaOH	14.10	17.75	10.90	7.25	43.60	29.00	−14.60

TABLE V

NaCl $C_1 = 25.00$cc

Solutions and conc.	C_2		A		$(A \times 100)/C_1$		D
	(a) Sept.	(b) Toget.	(a) Sept.	(b) Toget.	(a) Sept.	(b) Toget.	
N/20 NaCl	23.50	23.75	1.50	1.25	6.00	5.00	−1.00
+N/20 HCl	17.50	16.75	7.50	8.25	30.00	33.00	+3.00
N/20 NaCl	23.50	23.50	1.50	1.50	6.00	6.00	0.00
+N/40 HCl	16.5	15.50	8.50	9.50	34.00	38.00	+4.00
N/20 Nacl	23.50	24.25	1.50	0.75	6.00	3.00	−3.00
+N/20H_2SO_4	15.25	17.75	9.75	7.25	39.00	29.00	−10.00
N/20NaCl	23.50	23.75	1.50	1.25	6.00	5.00	−1.00
+N/40H_2SO_4	13.50	17.50	11.50	7.50	46.00	30.00	−16.00
N/20 NaCl	23.50	23.50	1.50	1.50	6.00	6.00	0.00
+N/20HNO_3	15.25	15.75	9.75	9.25	39.00	37.00	−2.00
N/20 NaCl	23.50	23.50	1.50	1.50	6.00	6.00	0.00
+N/40HNO_3	12.45	13.55	12.55	11.45	50.00	45.80	−4.20
N/20 NaCl	23.50	23.75	1.50	1.25	6.00	5.00	−1.00
+N/20$(COOH)_2$	7.95	12.50	17.05	12.50	68.20	50.00	−18.20
N/20NaCl	23.50	23.50	1.50	1.50	6.00	6.00	0.00
+N/40$(COOH)_2$	5.00	11.50	20.00	13.50	80.00	54.00	−26.00
N/20 NaCl	23.50	23.45	1.50	1.55	6.00	6.20	+0.20
+N/20 KOH	13.00	14.25	12.00	10.75	48.00	43.00	−5.00
N/20 NaCl	23.50	21.50	1.50	3.50	6.00	14.00	+8.00
+N/20 KOH	11.00	13.00	14.00	12.00	54.00	48.00	−6.00
N/20 NaCl	23.50	23.75	1.50	1.25	6.00	5.00	−1.00
+N/20Na_2CO_3	16.75	19.25	8.25	5.75	33.00	23.00	−10.00
N/20 NaCl	23.50	21.00	1.50	4.00	6.00	16.00	+10.00
+N/40Na_2 CO_3	15.50	17.50	9.50	7.50	38.00	30.00	−8.00
N/20 NaCl	23.50	23.00	1.50	2.00	6.00	8.00	+2.00
+N/20 NaOH	14.50	19.25	10.50	5.75	42.00	23.00	−19.00
N/20 NaCl	23.50	22.75	1.50	2.25	6.00	9.00	+3.00
+N/40 NaOH	14.10	18.00	10.90	7.00	43.60	28.00	−15.60

TABLE VI

$MgCl_2$ $C_1 = 25.00$cc

Solutions and conc.	C_2		A		$(A \times 100)/C_1$		D
	(a) Sept.	(b) Toget.	(a) Sept.	(b) Toget.	(a) Sept.	(b) Toget.	
N/20 $MgCl_2$	23.875	23.75	1.125	1.25	4.50	5.00	+1.00
+N/20 HCl	17.500	17.50	7.500	7.50	30.00	30.00	0.00
N/20 $MgCl_2$	23.875	23.50	1.125	1.50	4.50	6.00	+1.50
+N/20 HCl	16.500	16.50	8.520	8.50	34.00	34.00	0.00
N/20 $MgCl_2$	23.875	23.50	1.125	1.50	4.50	6.00	+1.50
+N/20H_2SO_4	15.25	18.50	9.750	6.50	39.00	26.00	−13.00
N/20 $MgCl_2$	23.870	23.25	1.125	1.75	4.50	7.00	+2.50
+N/40H_2SO_4	13.500	15.50	11.50	9.50	46.00	38.00	−8.00
N/20 $MgCl_2$	23.875	24.25	1.125	0.75	4.50	3.00	−1.50
+N/20HNO_3	15.25	16.25	9.75	8.75	39.00	34.00	−5.00
N/20 $MgCl_2$	23.875	24.00	1.125	1.00	4.50	4.00	−0.50
+N/40HNO_3	12.450	15.00	12.550	9.00	50.20	36.00	−14.20
N/20 $MgCl_2$	23.875	23.75	1.125	1.25	4.50	5.00	+0.50
+N/20$(COOH)_2$	7.950	14.25	17.05	10.75	68.20	43.00	−25.20
N/20 $MgCl_2$	23.875	23.50	1.125	1.50	4.50	6.00	+1.50
+N/40$(COOH)_2$	5.000	12.00	20.000	13.00	80.00	52.00	−28.00

TABLE VII

LiCl $C_1 = 25.00$cc

Solutions and conc.	C_2		A		$(A\times 100)/C_1$		D
	(a) Sept.	(b) Toget.	(a) Sept.	(b) Toget.	(a) Sept.	(b) Toget.	
N/20 LiCl	23.875		1.125		4.50		
+N/20HCl	17.500	18.25	1.500	6.75	30.00	27.00	−3.00
N/20 LiCl	23.875	24.00	1.125	1.00	4.50	4.00	−0.50
+N/40 HCl	16.500	17.00	8.500	8.00	34.00	32.00	−2.00
N/20 LiCl	23.875	24.00	1.125	1.00	4.50	4.00	−0.50
+N/20 H_2SO_4	15.250	19.25	9.75	5.75	39.00	23.00	−16.00
N/20 LiCl	23.875	24.00	1.125	1.00	4.50	4.00	−0.50
+N/40 H_2SO_4	13.50	18.50	11.50	6.50	46.00	26.00	−20.50
N/20 LiCl	23.875	23.75	1.125	1.25	4.50	5.00	+0.50
+N/20 HNO_3	15.250	14.00	9.750	11.00	39.00	44.00	+5.00
N/20 LiCl	23.875	23.50	1.125	1.50	4.50	6.00	+1.50
+N/40HNO_3	12.450	13.25	12.550	11.75	50.20	47.00	−2.80
N/20 LiCl	23.875	23.75	1.725	1.25	4.50	5.00	+0.50
+N/20$(COOH)_2$	7.950	17.25	17.050	7.75	68.20	31.00	−37.20
N/20 LiCl	23.875	23.750	1.125	1.25	4.50	5.00	+0.50
+N/40$(COOH)_2$	5.000	15.25	20.00	8.75	80.00	35.00	−45.00

TABLE VIII

$SrCl_2$ $C_1 = 25.00$cc

Solutions and conc.	C_2		A		$(A\times 100)/C_1$		D
	(a) Sept.	(b) Toget.	(a) Sept.	(b) Toget.	(a) Sept.	(b) Toget.	
N/20 $SrCl_2$	23.10	22.00	1.90	3.00	7.60	12.00	+4.40
+N/20HCl	17.50	17.25	7.50	7.75	30.00	31.00	+1.00
N/20 $SrCl_2$	23.10	21.50	1.90	3.50	7.60	14.00	+6.40
+N/40HCl	16.50	15.00	8.50	9.00	34.00	36.00	+2.00
N/20 $SrCl_2$	23.10	22.50	1.90	2.50	7.60	10.00	+2.40
+N/20 HNO_3	15.25	14.25	9.75	10.75	39.00	43.00	+4.00
N/20 SrCl	23.10	21.50	1.90	3.50	7.60	14.00	+6.39
+N/40 HNO_3	12.45	12.00	12.55	13.00	50.20	52.00	+2.00

TABLE IX

$CaCl_2$ $C_1 = 25.00$cc

Solutions and conc.	C_2		A		$(A\times 100)/C_1$		D
	(a) Sept.	(b) Toget.	(a) Sept.	(b) Toget.	(a) Sept.	(b) Toget.	
N/20 $CaCl_2$	23.50	23.00	1.50	2.00	6.00	8.00	+2.00
+N/20 HNO_3	15.25	15.30	9.75	9.70	39.00	38.80	−0.20
N/20 $CaCl_2$	23.50	22.85	1.50	2.25	6.00	9.00	+3.00
+N/40HNO_3	12.45	12.95	12.55	12.15	50.20	48.60	−1.62

TABLE X

Mixtures of KCl and NaCl

Solution and conc.	C_2		A		$(A \times 100)/C_1$		D
	(a) Sept.	(b) Toget.	(a) Sept.	(b) Toget.	(a) Sept.	(b) Toget.	
N/20 NaCl	23.50		1.50		6.00		
+N/20 KCl	23.19	23.20	1.81	1.80	7.24	7.20	−6.04
N/20 NaCl	23.500	22.275	1.50		6.00		
+N/40 KCl	22.94		2.06	2.725	8.24	10.900	−3.34
N/40 NaCl	23.40		1.60		6.40		
+N/20 KCl	23.19	22.86	1.81	2.14	7.24	8.56	−5.08
N/40 NaCl	23.40	22.80	1.60	2.20	6.40	8.80	
+N/40 KCl	22.94		2.06		8.24		−5.84

Interpretation of Results

Adsorption of a binary mixture is not completely additive. It is not the sum of the adsorption of the constituents of a mixture. It cannot be, for each effects a change in the adsorption of the other. The presence of a foreign substance may increase or decrease the adsorption of a substance and sometimes it has no effect and the value of the latter remains the same. If one of the substances of a mixture is adsorbed strongly, it takes place at the cost of the other. The second substance is said to be poisoned in technical language. This phenomenon is of importance in the manufacture of sulphuric acid by the contact process for the adsorbability of platinum is decreased in the presence of arsenic or its compounds and the platinum is said to be poisoned. In view of the present investigation this cannot be attributed to a special property of arsenic alone for other substances also behaved similarly. On the other hand, there may be substances which increase the adsorbability of platinum and investigations in this direction are worth trying for. This phenomenon is called by Michael Lach[1] and by Schmidt[2] the displacement principle and it follows no general law.

A few deductions that are possible from the above experiments may be summarized as follows.

If an increase or decrease of adsorption of two substances in a mixture takes place at one concentration then at a lower concentration the effect is much more in the same direction. For instance in a mixture of KCl and HCl an increase in adsorption of KCl is observed at both concentrations of HCl but the effect is much more at the lower concentration of HCl. In this particular case the change takes place in the positive direction; but there are cases where a decrease takes place and this follows the same law.

Both substances in a binary mixture are practically independent of the influence of one another. Such a phenomenon is observed in certain cases. This result is important for it throws some light over the nature of adsorption phenomenon itself. Adsorption is independent of the degree of dissociation of a substance.

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[1] Kapillarchemie, p. 184.

[2] Z. physik. Chem. 74, 689, (1910).

Both substances exert a mutual effect over one another corresponding to the "displacement principle". Many cases are seen where adsorption is lower. In a mixture of KCl and HNO_3 a decrease in adsorption takes place and the same effect can be found in case of other substances also.

Adsorbability of a substance is increased in the presence of a foreign body. It is interesting to find out that in a mixture with one ion common adsorption of one is increased at the cost of the other. The adsorption of KCl for instance is increased in presence of HCl.

How and why a particular change in a particular direction takes place cannot at present be answered. No generalisation regarding the behaviour of a substance in presence of another foreign substance can be made as far as adsorption is concerned. It is claimed by some that complex ion formation takes place when adsorption of a substance in a binary mixture is lowered, but no confirmation to it comes from other authors.

Experiments with Three Different Kinds of Wood Charcoal

The second part of the work was performed with wood charcoal. Charcoal was obtained from Tali, acacia, and mulberry wood. Methods of preparation and purification of charcoal are the same as in the case of animal charcoal with the difference that wood charcoal was prepared by burning wood in a small furnace in the laboratory.

Each experiment was carried on in the same way as before by bringing a solution of known concentration (N/40) in contact with two grams of charcoal and left for twenty minutes. After this time the solution was separated from the charcoal and its concentration was estimated by means of a standard silver nitrate solution. The adsorbed amount was found by subtracting the final concentration from the initial one. It was found that mulberry charcoal was best of the three kinds of charcoals examined.

Solutions

They were prepared in the same way as before N/40 concentration solutions were throughout used.

In this case also the method of representation is the same as in previous cases. C_1 and C_2 denote the initial and final concentration $(A \times 100)/C_1$ and A have the same meaning as before. The results obtained with different charcoals can be compared from the following tables.

TABLE XI

Tali Wood Charcoal

Solutions	C_1	C_2	A	$(A \times 100)/C_1$
HNO_3	25.00	18.50	6.75	27.00
H_2SO_4	25.00	20.80	4.20	16.80
HCl	25.00	19.55	5.45	21.80
KOH	25.00	18.40	6.60	26.40
NaOH	25.00	18.20	6.80	27.20
Na_2CO_3	25.00	20.35	4.625	18.50
NaCl	25.00	22.60	2.40	9.60
KCl	25.00	22.50	2.50	10.00
$MgCl_2$	25.00	24.15	0.85	3.40
$LiCl_2$	25.00	23.25	1.75	6.00
$SrCl_2$	25.00	23.15	1.85	7.40

TABLE XII

Acacia Wood Charcoal

Solutions	C_1	C_2	A	$(A \times 100)/C_1$
HCl	25.00	19.20	6.00	24.00
H_2SO_4	25.00	19.20	5.80	23.20
HNO_3	25.00	18.75	6.25	25.00
COOH	25.00	4.25	20.75	83.00
NaCl	25.00	23.40	1.60	6.40
KCl	25.00	23.15	1.85	7.40
$SrCl_2$	25.00	23.45	1.45	5.60
$CaCl_2$	25.00	20.85	4.15	15.60
$MgCl_2$	25.00	23.60	1.40	5.40
LiCl	25.00	24.125	0.875	4.375
$CaCl_2$	25.00	23.000	2.000	8.000

TABLE XIII

Mulberry Wood Charcoal

Solutions	C_1	C_2	A	$(A \times 100)/C_1$
HCl	25.00	18.75	6.25	25.00
H_2SO_4	25.00	19.625	5.375	21.50
HNO_3	25.00	17.250	7.750	38.75
CH_3COOH	25.00	16.75	8.25	41.25
KOH	25.00	17.875	7.125	28.50
NaOH	25.00	18.875	6.125	24.50
Na_2CO_3	25.00	17.10	7.90	31.60
KCl	25.00	22.00	3.00	12.00
NaCl	25.00	23.00	2.00	8.00
$MgCl_2$	25.00	23.70	1.30	5.20
LiCl	25.00	23.375	1.625	6.50
$SrCl_2$	25.00	23.25	1.75	7.00

TABLE XIV

Comparative Results of Adsorption Power of Charcoal of Tali, Acacia, Mulberry, and Animal Charcoal

Solutions	Acacia	Tali	Mulberry	Animal charcoal
HCl	24.00	21.80	25.00	34.00
H_2SO_4	23.20	16.80	21.50	46.00
HNO_3	25.00	27.00	38.75	50.20
$(COOH)_2$	83.00			20.00
CH_3COOH			41.25	
NaOH		27.20	24.50	43.60
KOH		26.40	28.50	56.00
Na_2CO_3		18.50	31.60	38.00
NaCl	6.40	9.60	8.00	6.40
KCl	7.40	10.00	12.00	8.24
$MgCl_2$	5.40	3.40	5.20	6.00
LiCl	4.375	6.00	6.50	5.00
$CaCl_2$	15.60	13.40		9.00
$SrCl_2$	5.80	7.40	7.00	7.80

Interpretation of Results

1. Adsorption power varies with the nature of substance. It also varies with different charcoals.

2. On the whole mulberry charcoal appears to be the best of the three so far as regards adsorption is concerned.

Conclusions

They may be summarised briefly as follows:—

1. Temperature has very little effect on adsorption of a substance by charcoal. Increase of temperature produces an increase in adsorption.

2. With an increase in dilution of a substance in solution, the relative adsorption amount increases, but at higher concentration the absolute amount of adsorption is greater than at lower concentration.

3. Adsorption depends to some extent upon the chemical nature of a substance. NaCl, KCl, LiCl, $MgCl_2$ all belonging to the same group in the periodic table possess lower adsorption values than $SrCl_2$ or $CaCl_2$.

4. In adsorption of binary mixtures three things may be observed:—

(a) Presence of a foreign substance may have no effect on the adsorption of another substance and so adsorption depends very little on ionization of a substance.

(b) A substance may be adsorbed less in presence of another substance, than it would be if it were alone in solution. In other words adsorbent may be poisoned with regard to one substance by the presence of another substance.

(c) Adsorption of a substance may be increased in the presence of another substance or of one may be increased at the cost of the other.

5. Adsorption of mixtures follows no general rules and so the effect of one substance over the adsorbability can not be predicted.

6. Adsorption of wood charcoal approximates or even exceeds to that of animal charcoal when the former has undergone a heat treatment.

7. With some exceptions the adsorption numbers with different charcoal can be arranged in the same order. This shows that adsorption also depends upon the chemical properties of a substance.

8. The different kinds of charcoal have different adsorption power. Mulberry charcoal adsorbs more than that from Tali or acacia.

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THE PHOTO-CHEMICAL PROPERTIES OF CUPROUS OXIDE

BY ALLEN GARRISON*

In a report[1] entitled "The Behavior of Cuprous Oxide Photo-voltaic Cells" the changes in potential of various cuprous oxide electrodes when illuminated were explained by the assumption that the oxide becomes more soluble to an extent which is proportional to the intensity of illumination. A number of determinations of normal electrode potentials and photo-potentials led to this conclusion but in view of the fact that this postulates a distinctly new type of photo-chemical reaction a careful investigation of the case has been made by the conductivity method to obtain evidence from a source other than that of electromotive force measurements.

The Experimental Procedure

The purpose of this investigation was to determine whether or not a system consisting of pure water saturated with cuprous oxide would have its conductivity increased on illumination as the theory apparently demands. The solubility of cuprous oxide was found to be approximately 10^{-5} moles per liter. In order, therefore, to make an observation of a photo-chemically induced change in conductivity of such a system a finely divided suspension of the oxide in pure water was prepared of density sufficient to permit the light to penetrate several centimeters of the liquid.

Water was purified by triple distillation, first from an alkaline permanganate, second from dilute sulfuric acid and finally from very dilute potassium hydroxide. The still and receiver were of Pyrex glass and the condenser of block tin. Water thus prepared had a conductivity of 1.05×10^{-6} reciprocal ohms.

C. P. powdered cuprous oxide was washed with the conductivity water a large number of times until the suspension gave constant conductivity at 25°.

A Pyrex glass cell having platinized electrodes was prepared for the conductivity measurements. The platinum wires were flattened into a ribbon and the edges sharpened before they were sealed into the glass thus providing a water tight seal without the use of any substance in the cell other than Pyrex glass and platinum. The lower part of the cell consisted of a bulb, containing the vertical electrodes, and a large tube in the form of a ring leading from the top to the bottom of the bulb. A glass vane driven by a small motor was placed in this tube so that the suspension could be circulated through the bulb between the electrodes. The cell was placed in a thermostat and kept at 25° while measurements were being made. The thermostat was also glass enabling the cell to be illuminated by a beam of white light from a 500 candle

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[1] J. Phys. Chem. 27, 601 (1923)

power tungsten lamp. Measurements of conductivity were made with a high-grade Wheatstone bridge of standard make having variable air condensers for balancing the cell capacity.

The conductivities of the suspensions varied from 4.40×10^{-6} to 6.65×10^{-6} reciprocal ohms, giving for the conductivity of the oxide 3.35×10^{-6} to 5.60×10^{-6}. If the mobility of the cuprous ion is taken to be the same as that of the cupric ion this would give for the solubility of the oxide 1.5×10^{-5} to 2.5×10^{-5} moles per liter. These values are large compared to those obtained by electrode potential methods, due probably to the presence of cupric ions formed either by electrolytic equilibrium or atmospheric oxidation.

The Results of Illuminating the Cuprous Oxide Suspensions

Within the range of sensitivity of the bridge, 1 part in 5000, no change in the conductivity of the cuprous oxide suspensions could be observed in white light of approximately sun light intensity. This is apparently contrary to the theory under discussion since the effects observed on the electrode potentials would demand an observable change in conductivity. The conditions are not strictly comparable, however, because the electrodes used in the previous investigation were copper coated with a thin layer of cuprous oxide. The presence of the copper is apparently important. Its influence on the solubility of the oxide is probably negligible but, in view of the fact that the amount of substance in solution is small and the area of the finely divided particles large, an induced photo-potential could not be neglected due to the electrostatic attraction of the particles and the removal of ions in the formation of the electrolytic double layers. It was found that the density of the layer of oxide which determined the amount of metallic copper in contact with the electrolyte had a marked influence on the photo-potential of the electrode.

The Influence of the Amount of Copper on the Photo-Potential

Table I gives results which were discovered in a qualitative way in the previous work.

TABLE I

The Influence of the Density of the Oxide Layer on the Normal Potential and the Photo-Potential of the Copper Electrode

(1) No.	(2) Time coated	(3) E_{Cu+}	(4) dE	(5) dE_{ν}	(6) E_{H+}
1	5 sec.	−0.156	+	+0.050	−0.831
2	30	−0.155	+	+0.004	−0.831
3	60	−0.144	−0.021	−0.001	−0.832
4	120	−0.112	−0.024	−0.023	−0.831
5	5 min.	−0.110	−0.065	−0.040	−0.831
6	Repeatedly.	−0.102	−0.200	−0.070	−0.832

Six copper electrodes indicated by the numbers in column 1, were coated with different densities of cuprous oxide by placing for a short time in a dilute solution of cupric chloride and completely hydrolyzing the resultant layer of cuprous chloride in running distilled water. The density of the resultant oxide depended on the time of forming the chloride as indicated in column 2.

The electrodes were then placed in 0.1N K_2SO_4 solution and the potential of each in the dark compared to that of a 0.1N calomel electrode. These values are recorded in column 3. The electrodes were increasingly positive in the order of increasing density of cuprous oxide deposit. The hydrogen ion concentration in the K_2SO_4 solution was measured by a platinized gold electrode saturated with hydrogen gas at atmospheric pressure. Its potential was constant to 0.001 volt for all the determinations as shown in column 6. From the simple mass law relations there was thus at equilibrium a constant concentration of cuprous ions in the vicinity of each electrode. From the relation

$$E = e_{Cu}^{+} + \frac{RT}{nF} \log \frac{(Cu^{+})}{(Cu)}$$

it is evident that the variations in E in column 3 are due to a variation in the "concentration" of the metallic copper in contact with the electrolyte. As the oxide coating was thickened the underlying copper became isolated from the solution and its active concentration diminished. As proof of this, electrodes 5 and 6 were scratched with a large number of fine lines to expose the underlying copper and their normal potentials reduced almost to those of Nos. 1 and 2. This affords experimental evidence for the assumption of "diluted copper" made in the previous investigation and based on different considerations.

The initial changes in potential induced by white light are recorded in column 4 and the change after 5 minutes exposure to the light in column 5. The important thing in this connection is the fact that the diminution in the amount of copper is accompanied by a large negative photo-potential.

The particles of cuprous oxide used in the conductivity measurements contained an infinitely small amount of metallic copper. Each particle acting as an electrode would develop a negative charge relative to the electrolyte on illumination. The resultant electrolytic double layer would require positive ions of the solution to balance the charge at the surface of the solid. Therefore, even though cuprous and hydroxide ions were liberated by the radiation, the cuprous ions may be held in the double layer as well as some of the more mobile hydrogen ions thus preventing an increase in conductivity in the body of the electrolyte. In order to test this theory, suspensions were made of copper having a thin oxide deposit of the electrode type having a positive rather than a negative photo-potential. Powdered copper just fine enough to be held in suspension by gentle stirring was coated with oxide by the method already described. After the chloride had been completely hydrolyzed the suspensions were washed in pure water to constant conductivity and placed in the apparatus described above.

The Results of illuminating the Copper-Cuprous Oxide Suspensions

Suspensions of copper having a thin deposit of copper oxide were found to have a higher conductivity in light than in the dark. The difference is large compared with any temperature effect which could have been induced by the light. During the observation of the effect of light the temperature of the cell did not vary more than 0.1°. Table I shows the magnitude of the light effect compared with the temperature coefficient of three different observations. If the effects observed were due to the heating effect of the light there would have been a rise in temperature of at least 2°, an occurrence which could not have escaped notice.

TABLE II

The Temperature Coefficients and Light Effects of the Copper—Copper Oxide Systems

Conductivity in Dark at 25°	Conductivity in Dark at 26°	Conductivity in Light at 25°
7.16×10^{-6}	7.49×10^{-6}	8.00×10^{-6}
4.41 "	4.51 "	4.62 "
5.08 "	5.22 "	5.45 "

The magnitude of the light effect was different for different suspensions. In the case of suspensions having dense coatings of oxide the effect of light was small. Suspensions prepared in the same manner as electrodes Nos. 5 and 6 in Table I were practically unchanged by light. These had the appearance of the pure oxide suspensions, while the more sensitive ones, having been coated in a manner similar to electrode No. 1 in Table I, had the color of brass.

Experiments were performed in which the platinum electrodes of the conductivity cell were kept in the dark and the suspension illuminated at a point in the tube just above the electrodes. As the liquid circulated through the tube it passed first through the beam of light and then between the electrodes. Conductivity changes were observed in this way also indicating that the effect was not at all associated with the fact that the light fell on the cell electrodes.

In other experiments the suspension was permitted to settle to the bottom and the clear liquid free from solid particles was exposed to the light. No change in conductivity was observed under these conditions.

Systems in which the Light reduces the Conductivity

It was noticed that a copper suspension having a cuprous chloride coating only partially hydrolyzed to the oxide had its conductivity reduced on illumination. Hydrochloric acid is formed during hydrolysis and a state of equilibrium may be reached with both solids present unless the acid is removed by continued washing. Under these conditions the suspension had a coating of the mixed chloride and oxide and had therefore established the following equilibria:

$$Cu_2Cl_2 \text{ solid} \rightleftarrows Cu_2Cl_2 \text{ solute} \rightleftarrows 2\,Cu^+ + 2\,Cl^- \qquad (1)$$

$$Cu_2O \text{ solid} \rightleftarrows Cu_2O \text{ solute} \rightleftarrows 2\,Cu^+ + O^= \qquad (2)$$

If the light shifts the reaction (2) to the right, reaction (1) will move to the left and the result may be written in one equilibrium, thus

$$Cu_2Cl_2+H_2O \overset{\text{light}}{\leftarrow} \overset{\text{dark}}{\rightarrow} Cu_2O+2\,H^+ +2\,Cl^- \qquad (3)$$

The conductivity of this system was relatively large due to the fact that the cuprous chloride is more soluble than the cuprous oxide and an appreciable amount of HCl must be present. The conductivity was reduced as much as 15% in white light of approximately sun light intensity. Thus one suspension had a conductivity of 26.0×10^{-6} in the dark and 22.1×10^{-6} in the light. When this suspension was washed repeatedly its conductivity decreased and it began to behave like the suspensions given in Table 2. The original condition represented in reaction (3) was restored by adding a trace of HCl.

The photo-chemical diminution of hydrogen ion concentration represented in reaction (3) was also observed by placing a hydrogen electrode in the suspension and comparing its potential with that of a 0.1N calomel half cell. During illumination the hydrogen electrode became more negative by approximately 0.03 volts. This effect was observed only qualitatively since the hydrogen at atmospheric pressure slowly displaced the cuprousions from solution.

Discussion

The results of this investigation may be explained by the single assumption that the equilibrium constant of the reaction (2) alters in light so that the oxide apparently becomes more soluble. This was also the assumption made in developing the theory of the photo-voltaic cells which may be briefly summarized as follows:

On illumination reaction (2) was supposed to shift to the right thereby simultaneously increasing the concentration of both the cuprous and the hydroxide ions.

Case (1). A positive photo-potential results when the electrode potential is determined by the reaction:

$$Cu^+ \rightleftarrows Cu + (+) \qquad (4)$$

The reaction determining the potential of the electrode at equilibrium is that reaction which may proceed from a given unstable state to the equilibrium state with the smallest changes in the concentrations of the reactants. Case 1 is realized when metallic copper and solid cuprous oxide are present.

Case (2). A negative photo-potential results when the potential is determined by the reaction,

$$2\,O^= \rightleftarrows O_2+(=) \qquad (5)$$

Reaction (4) can not determine the potential of the electrode when the amount of copper present is infinitely small for then its concentration varies with the smallest current. Case 2 was realized by removing the metallic copper. A temporary negative photo-potential may also be induced by the side reactions,

$$Cu^+ \longrightarrow Cu+(+) \longrightarrow Cu^{++} + (-)$$

A more complete discussion of this theory will be found in the previous paper.

The system $H_2O-Cu-Cu_2O$ corresponds to Case 1 and the increased conductivity on illumination may be attributed to the production of more Cu^+ and OH^- ions. The positive photo-potential would not mask the change in conductivity.

The system H_2O-Cu_2O corresponds to Case 2 in which experiments have revealed a large negative photo-potential. It is probable that this potential change prevents the detection of the change in solubility.

The system $Cu_2Cl_2-Cu_2O-Cu-H_2O$ provides a new example of a consecutive photo-chemical reaction. Reaction 2 is the primary photo-chemical change while reaction 3 represents the consecutive one.

The conductivity method of observing these reactions quantitatively suffers from several disadvantages which the electrode potential method evades. In the first place traces of impurities influence the conductivity method but not the electrode potential method. The cell constant cannot be accurately estimated when metallic suspensions are employed since the particles themselves conduct the current and thus reduce the effective distance between the electrodes. Furthermore, uniform illumination throughout a suspension is impossible since the intensity at any point depends on the density and thickness of the suspension traversed. The method is valuable, however, in a qualitative way in furnishing additional evidence that the solubility of the cuprous oxide increases in light.

This is apparently a direct confirmation of the theory of Baly[1] in which he postulates an opening of the molecular "force fields" by radiation in the same manner in which they are opened by a solvent. We may imagine that the separation of the negatively charged ion is similar to the separation of an electron under the influence of the radiation.

Summary

The conductivity of a suspension of cuprous oxide in pure water is not influenced by white light.

The conductivity of a suspension of copper coated with a thin layer of cuprous oxide is increased by white light. This has been distinguished from a temperature effect.

Evidence for the variation of copper concentration was obtained using electrodes coated with different thicknesses of cuprous oxide, the photo-potentials were also shown to depend on the amount of copper.

The system $Cu_2Cl_2-Cu_2O-Cu-H_2O$ has a higher resistance in the light than in the dark and affords a new example of a consecutive photochemical reaction.

The results may be explained by the assumption that cuprous oxide becomes more soluble in light. This is apparently a confirmation of the theory of Baly.

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[1] Astrophys. J. 42, 4-71 (1915); J. Am. Chem. Soc. 37, 979-993 (1915)

THE SOLUBILITY OF ATMOSPHERIC GASES IN SOLUTIONS OF AMMONIUM CHLORIDE

BY J. H. COSTE AND E. R. ANDREWS

The solubility of atmospheric oxygen in solutions of various salts was determined by C. G. MacArthur[1]. His results for the halides of alkali metals are of the order one would expect, having regard to the solubility of oxygen in sea water but those for ammonium chloride solutions are very remarkable. They are for a temperature of 25°C.

Concentration	M	$\frac{M}{4}$	$\frac{M}{8}$	$\frac{M}{\text{Infinity}}$
Solubility of oxygen in cc per litre	0.07	1.16	2.31	5.78

In discussing these results MacArthur says: "Another fact to be noted is the marked effect of ammonium chloride on the solubility of oxygen. It raises with the concentration, but the decrease in solubility is extremely large. At first it was thought to be due to a combination of the ammonium chloride with the manganous chloride,[2] thus preventing the manganous compound from being oxidized by the oxygen in solution. This was shown not to be true by adding the ammonium chloride to water containing the usual amount of the alkaline iodide and manganous chloride solutions and finishing the determination as usual. This gave an amount of oxygen that distilled water usually contains. Though it is more likely that the ammonium chloride so influences the oxygen that it is not available to oxidize the manganous hydroxide, it is still possible that the ammonium chloride markedly decreases the amount of oxygen in solution."

It appears, therefore, that MacArthur had some doubt as to the real significance of his results although their accuracy appears to have been accepted by other authors.

If ammonium chloride in relatively dilute solutions really conferred this property upon water much use could be made of the fact in gas analysis and manipulation.

The general similarity in behaviour of ammonium chloride and the chlorides of the alkali metals raises a strong presumption that there is some explanation of MacArthur's results other than a specific effect on the solubility of oxygen. The use of ammonium chloride in preventing the co-precipitation of hydroxides of manganese, zinc, nickel and cobalt with those of iron, chromium and aluminum is well known to most students. The experiment cited by MacArthur only shows that ammonium chloride will not re-dissolve and re-

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[1] J. Phys. Chem. 20, 495 (1916).

[2] Winkler's manganous process for the determination of dissolved oxygen.

duce manganic oxide when it has formed, as it does very rapidly in Winkler's process. It does not show that a manganese ammonium complex is not found. The interaction of manganous and ammonium compounds has been studied by W. Herz[1] and is referred to in some of the larger text-books of inorganic chemistry.

We have experimented with ammonium chloride solutions and find that the salt undoubtedly exerts a considerable retarding effect on the precipitation of the hydroxides of manganese, the solution remaining clear for some time and only yielding a considerable precipitate, apparently all manganic, after some hours.

Solutions of ammonium chloride in distilled water through which air had been bubbled for some hours, were examined (a) by Winkler's manganous process, using 70 cc of the solution and 0.3 cc of each of the reagents (b) by Winkler's gasometric process in which the oxygen and nitrogen dissolved in the water are evolved by a current of carbon dioxide generated in the water from calcite by means of hydrochloric acid[2]. It will be seen from the table below that the content of oxygen and nitrogen in ammonium chloride solutions differs but little from that in sodium or potassium chloride solutions of the same molar concentration.

Molar Concentration of NH_4Cl	Temperature of Saturation	Dissolved Gases ccs per litre		
		Winkler's Gasometric Process		Winkler's Manganous Process
		Nitrogen and Argon	Oxy-gen	Oxygen
2 M	22	7.79	3.93	1.6 (overnight)
M	19	10.15	5.70	2.6 (20 hours)
	20	10.29	5.04	
$\frac{M}{2}$	20	10.65	5.48	5.46 (18 hours)

No separation of hydroxide of manganese was observed in six hours with the 2 M solution, some turbidity but no precipitate was observed in 4 hours with the normal solution whilst the M and M/2 gave some precipitate at once and action was complete in eighteen hours.

The ammonium chloride solutions were sought to be saturated with the gases of air by passing a fine stream of bubbles for about 3 hours. It is not suggested that the figures in the above table are of the highest accuracy but they show conclusively that the order of solubility of the gases of air in ammonium chloride is very different from that given by MacArthur and also the inapplicability of the manganous process in presence of large proportions of ammonium salts.

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[1] Z. anorg. Chem. **21**, 243; **22**, 279.

[2] L. W. Winkler: Z. anal. Chem. **40**, 523 (1901).

NEW BOOKS

A Treatise on Chemistry. *By Sir Henry Roscoe and C. Schorlemmer. Vol. II, Part I. Sixth edition completely revised by B. Mouat Jones and others. 21×15 cm; pp. xv+1565. New York and London, 1923. Price: $15.00.* "In the ten years which have elapsed since the publication of the fifth edition of this book much new knowledge has been obtained of the chemistry of the metals and of their compounds. An endeavour has been made to incorporate the most important of this new material in the present edition while bringing the rest of the volume up to date. Great advances have been made in our fundamental ideas of atomic and molecular structure, of valency and of chemical affinity, and in the interpretation of the Periodic Law. This has been largely a result of the rapid development of the science of radio-activity and the 'new physics' and of the introduction of two new methods of investigation—positive ray analysis and X-ray spectroscopy. So rapid has been this advance, and so much new data are being acquired daily, that in a work of this kind, devoted mainly to a systematic account of the metals and their compounds, anything like a complete account of the new theories would be out of place. Only the outstanding results of the 'new chemistry' have therefore been referred to, while the general style and character of the book have been maintained," p. IX.

"The decomposition of the alkalis by Davy in 1807 made chemists acquainted with substances of an entirely new character. Although the bases of soda and potash agreed with metals in opacity, lustre, malleability, conductive powers as to heat and electricity, and in their qualities of chemical combination, and were classed by Davy himself with the metals, yet, inasmuch as they were lighter than water, they were not considered by many chemists to be metals proper. In 1808 Erman and Simon attempted to revive the old distinction between true metals and substances resembling metals by proposing for the new substances the name of metalloids. This proposal, however, was not generally accepted, and the elements were from this period classed in two groups, the non-metals and the metals, the newly coined term, metalloid, being applied, or rather misapplied, by Berzelius in 1811 to designate the former of the two classes, in which sense it is still sometimes employed. It soon became evident that the separation of the elements into these two groups was not a logical one, since no satisfactory basis of classification could be obtained. With the discovery of the alkali metals a high specific gravity had ceased to be characteristic, and the property of metallic lustre soon shared its fate. Thus tellurium, discovered in 1782, was grouped with the metals because of its lustre and specific gravity. Its close chemical analogy with sulphur, however, which was pointed out by Berzelius in 1832, clearly indicated that these two elements belonged to the same class.

"In the same way, every property supposed to be characteristic of a metal has been found to be shared by some one or other non-metallic substance, or to be absent from some otherwise well-characterised metal. Thus opacity, and the power of conducting electricity well, were long deemed essential properties of a metal; but we now know that, in very thin layers, metals such as gold and silver are transparent, whilst several non-metals, such as graphite, and selenium, in one of its modifications, conduct electricity like metals," p. 4.

In view of the recent work to the effect that carbon and graphite have the same true density, it is interesting to note, p. 19, that in 1874 "Weber further showed that the allotropic modifications of a substance at low temperatures possess different specific heats, but that this difference diminishes as the temperature rises, and at last altogether disappears. For example, Regnault concluded from his experiments that the specific heat of amorphous carbon was different from that of the two other modifications. Weber has, however, distinctly shown that this is not the case, but that carbon exists in only two thermal modifications, (1) opaque, (2) transparent. These thermal differences occur only at low temperatures, and when a high temperature is reached no variation is observed."

The discussion of Dulong and Petit's law is summed up, p. 23, to the effect that "taking into consideration the results thus deduced from the molecular heats of compounds, it appears that the elements which possess an exceptionally small atomic heat at temperatures below 100° have low atomic weights and, with the exception of glucinum, are non-metals. All the non-metals the atomic weights of which are high, as well as the remaining metals, agree approximately with Dulong and Petit's rule below 100°."

In regard to Werner's theory the authors say, p. 39, that "this theory has proved of great value in the classification of the complex derivatives of the metals, and numerous applications of it will be found under the separate metals. The more recent development of the theory has taken the form of prediction of the existence of isomerides, and the predictions have been verified in a striking manner. The representation of the six coordinated groups or atoms as arranged in space round the central atom in the relative positions of the angles of an octahedron, leads to conclusions as to the existence of *cis-* and *trans-* isomerides in certain cases, and of optical isomerides in others. Such isomerides have now been isolated, and this fact gives strong support to Werner's views."

"The indifference of a supersaturated solution to crystals of non-isomorphous salts can readily be shown experimentally. A supersaturated solution of sodium acetate, prepared as described above, is poured gently on to the surface of a supersaturated solution of sodium thiosulphate, made by simply melting the crystals of the hydrated salt in a long test-tube. If, after cooling, a crystal of sodium thiosulphate is dropped into the tube, it falls through the lighter solution of sodium acetate without inducing crystallisation, but causes immediate crystallisation of sodium thiosulphate when it comes into the heavier solution of sodium thiosulphate. A supersaturated solution of magnesium sulphate may be made to crystallise by adding either magnesium sulphate itself, or any one of the isomorphous sulphates of iron, zinc, nickel, etc., whilst sodium sulphate, sodium chloride, etc., have no action upon it. Supersaturated solutions of sodium sulphate crystallise very readily when exposed to the air, and it has been shown that this is due to the presence of minute crystals of this salt in the atmosphere," p. 130. On p. 151 one reads that "in the year 1845 Wm. Allen Miller published the results of experiments on the spectra of coloured flames, together with drawings, but owing to the fact that in these researches a luminous flame was made use of, the representations of the several spectra are wanting in clearness and individuality. Swan was the first to point out that the bright yellow line coincident with Fraunhofer's D, which was seen in every flame, is caused by the presence of sodium salts, and it is to him that we are indebted for the discovery of the extreme delicacy of the sodium reaction, and for the proof of the universal distribution of this element." It seems incredible that it should have been fifteen years after this that Bunsen and Kirchhoff discovered the fundamentals of solar spectroscopy. No mention of Weiser's work is given under flame spectra, pp. 154, 182, although dissociation is postulated.

It is interesting to note, p. 161, that "it is often found that variation in the pressure of the gas, or of the intensity of the discharge, produces a variation in the relative intensity of the lines of the spectrum. Thus, in helium at a pressure of 7-8 mm, the yellow lines are the most conspicuous, and the gas glows with a yellow light; whilst, at a lower pressure the most conspicuous line is in the green, and the gas glows with a greenish-coloured light."

Sorby states, p. 177, that "wines of different vintages may be distinguished by a variation in their respective absorption spectra." This could be true without having to admit that one could identify vintages by their absorption spectra.

The sodium metaphosphates, which were first discovered by Graham, "exist in a large number of modifications, which all have the empirical formula $NaPO_3$; but their molecular formula is probably in most cases some multiple of this. Great uncertainty exists as to the true molecular weights of the various salts," p. 283.

"An impure arsenate of sodium is prepared on a large scale by dissolving arsenious oxide in caustic soda, and adding sodium nitrate; the solution is boiled down, and the residual mass heated in a furnace until it appears to be perfectly dry. This product is largely used in calico-printing as a substitute for cow-dung, which was formerly employed in clearing the cloth before mordanting. The mordant consists of a solution of acetate of either aluminum or iron, and the cloth, after having been printed with these mordants, is hung up and exposed to air. In this, which is termed the ageing process, a portion of the acetic acid evaporates, leaving basic acetates of iron and aluminum firmly attached to the fibre of the cloth. A portion of these salts is, however, mixed up with the thickening or starch which must be added to the mordant in order that the impression shall be sharp. To remove this excess of unfixed mordant, the cloth is subjected to a peculiar treatment termed the dunging process. For this purpose it will not answer merely to wash the cloth in pure water, because the soluble portion of the mordant is then removed from the printed pattern, but attaches itself again to the unmordanted cloth, which it is intended should remain white. Long ago it was observed by the native dyers and calico-printers in India that, if cow-dung be added to the wash water, the excess of mordant can be removed without any staining of the cloth occurring. The action of the cow-dung in this process has not yet been satisfactorily explained, but experience has shown that sodium arsenate solution acts in a similar way, and at the present time the old process is generally superseded by the use of what is known in the trade as dung substitute," p. 285.

"Ultramicroscopic examination of sodium silicate solutions show that they are two-phase systems in which the dispersed phase is negatively charged. . . . Silicate of soda is employed in fixing fresco colours by the process of stereochromy. It is employed as a cement in the manufacture of artificial stone. This is made by mixing the solution with sand and lime; it is likewise used as a cement for joining the broken surfaces of porcelain, stone, etc. Another purpose for which soluble glass is employed is as an addition to cheap soap. The so-called silicated soap was patented early in the last century and was subsequently largely made by William Gossage, who also took out a patent for its manufacture; it is now prepared in large quantities by adding a solution of this compound to the soap whilst settling," p. 294.

Potassium meta-silicate, K_2SiO_3, forms a glassy mass which deliquesces on exposure to moist air. "It also absorbs carbonic acid from the air, and is gradually transformed into a transparent jelly which shrinks together in time and, after some weeks, becomes hard enough to scratch glass. It is probable that opal and flint are formed in some similar manner (Kuhlmann)," p. 374.

Apparently ammonium carbonate was once rather an expensive substance, p. 405. "Even up to the end of the 17th century 'English drops,' which were really nothing more than carbonate of ammonia mixed with an ethereal oil, were sold at high prices, and it was stated by some that the volatile alkali contained in this substance was prepared by the destructive distillation of silk, whilst others gave the remarkable receipt that 5 lb. of skulls of persons who had been hanged, or had otherwise come to an unnatural end, must be distilled with 2 lb. of dried vipers, hartshorn and ivory."

"The name of chrysocolla occurs in old writers and serves to describe the most diverse bodies. The word originally was used to signify the substance employed for soldering gold; this, being prepared from urine, was probably microcosmic salt, which became coloured blue in the act of soldering gold to copper or brass. The word then came to be used for any green or blue substance, especially such as contained copper; the confusion thus created was that all blue or green minerals, such as emerald and malachite, as well as substances which were employed for soldering, were termed chrysocolla. Brochant, in the year 1808, first proposed to confine the use of the name to this particular mineral," p. 456.

One would like very much to know why latitude has an apparent effect on the fineness of native gold, p. 510. "The Australian is, as a rule, much purer than the Californian gold, but it is a singular fact that the average fineness of the gold found in the several Australian colonies shows a regular depreciation as we advance northwards. Thus the average fineness of Victorian gold is about 960; that of the New South Wales gold is 935, while still further north in Queensland the average fineness is 872, and Maryborough gold contains only 85 percent of gold and as much as 14 percent of silver."

"The manufacture of glass appears to have been discovered by the Egyptians, although the ancients themselves attributed the discovery of glass-making to the Phoenicians. Glass vessels of various sizes, both colourless and coloured, have been found in Egyptian tombs which belong to an age prior to that in which the Phoenicians occupied themselves with glass-making. Indeed, the latter nation appear rather to have been engaged in exporting the glass made in Egypt, and especially at Thebes, to different parts of the ancient world, than to have established any original manufacture of their own. In the tombs of Beni Hassan near Thebes, which were built more than 2000 years B.C., we find paintings representing Egyptians carrying on the processes of glass-blowing. From these, as well as from the glass vessels which are found in the tombs, it appears that the Egyptians were not only acquainted with the art of glass-making and of working in glass, but likewise with that of cutting and colouring glass, by which they imitated precious stones," p. 585.

"The glass industry was introduced into Russia in the 17th and 18th centuries by German and Bohemian workmen. In the United States the same manufacture appears to have been established by Robert Hewes, a citizen of Boston, who erected a glass-house in the forest which existed in New Hampshire. The manufacture of Hewes does not seem to have been successful, and in 1800 another attempt was made to establish a glass-house at Boston, which also failed, until a German of the name of Lint took charge of the works in 1803, and the State of Massachusetts agreed to pay a bounty on all glass manufactured by him," p. 588.

Liquid mercury "is transparent when in very thin films, and transmits violet-blue light (Melsens). When a powerful stream of water is poured from a height of a decimetre on a mass of from 15 to 20 kilos. of mercury, bubbles of the metal, of about 1 cm. in diameter, are seen swimming on the surface of the water. These consist of very thin films of mercury through which blue light is transmitted: they soon burst and leave behind a very small globule of the metal," p. 697.

Gallium melts at about 30°; but the molten metal remains liquid indefinitely even at 0° until touched with a small fragment of solid gallium, p. 773. The color relations of the three forms of titanium dioxide are a bit puzzling. Rutile is a brown or reddish color, anatase is brown or black, while brookite is steel blue, p. 837. There is a surprising variation in the composition of meteoric irons, from 91% iron and 8% nickel as the one extreme to 64% iron and 34% nickel as the other. The authors apparently do not accept Hartley and Ramage's claim of having observed a fall of meteoric dust in Dublin for they say, p. 1212, that "finely divided meteoric iron is constantly falling from extra-terrestrial space on to the earth: the occurrence of this meteoric dust has been observed in Sweden and in the snowfields of Northern Siberia, the snow enclosing black magnetic particles which contain cobalt as well as iron. Similar particles of meteoric dust, consisting of metallic iron, have been found by Murray, of the Challenger expedition, at great depths in mid-ocean. It is only under conditions such as the above that it is possible to detect this fine meteoric dust, in consequence of the enormous accumulation elsewhere of terrestrial dust."

On p. 1272 we read that "ferric hydroxide forms a compound with sugar which is soluble in water. This fact is of great importance to sugar refiners, as this compound destroys the crystallising power of sugar, and therefore increases the quantity of molasses formed." One wonders whether all substances which are peptized by sugar prevent the crystallization.

"Hofmann and Resenscheck suggest that the cause of the intense colour of the ferric ferrocyanides is the presence in the same molecule of ferrous and ferric iron atoms; thus derivatives of the type $Fe^{II}K_2(Fe^{II}Cy_6)$ are colourless, whereas $Fe^{III}K(Fe^{II}Cy_6)$ is Prussian blue. They point out that similar intense colour is present in many other compounds containing an element in different stages of oxidation. For example, sulphur sesquioxide, S_2O_3, is of a deep indigo blue colour, whereas both sulphur dioxide and trioxide are colourless; red lead, in the same way, is more highly coloured than litharge or the dioxide; the tungsten bronzes furnish another example," p. 1315.

"In 1881 the Swiss Government introduced a new issue of 20 centime pieces made of pure nickel. These coins have proved so successful that many other nations have introduced pure nickel coinage to replace silver, bronze, and even cupro-nickel. At the end of 1912, Switzerland, Austria, Italy, France, Serbia, Montenegro, Mexico, Turkey and Siam had adopted the metal for small coinage, and about a thousand million pieces were in circulation. The advantages of a nickel coinage, and especially of pure nickel, are many. First, the metal is more valuable than copper, and consequently, for the same value, the coins can be of smaller size. Secondly, it is extremely tough, and the coins wear so well that replacement costs are extremely small. There is practically no deterioration in the Swiss coins which have been in circulation for forty years. Thirdly, owing to its hardness, nickel is very difficult to work, extensive plant and machinery and highly skilled labour being required for the production of coins, so that the manufacture of counterfeits would not be an attractive and profitable business. Lastly, nickel provides a clean and beautiful coinage. It has a brilliant surface, takes the impress of the die most distinctly and permits, therefore, of the most elaborate designs, a further difficulty thus being placed in the way of the counterfeiter," p. 1361.

Finely divided nickel is now being used as a catalyst for the removal of carbon disulphide from coal-gas, thus reducing its sulphur content considerably, p. 1368. "The catalyst is made by impregnating balls of fireclay with a nickel salt. They are filled into towers and the salt is reduced to metal in a stream of coal-gas. The towers are kept at a temperature of about 400°, and the gas to be purified is passed through. The carbon disulphide is decomposed, the carbon being deposited and the sulphur uniting with the hydrogen of the gas to form hydrogen sulphide, which is then absorbed by ferric oxide in the usual manner. After running for some weeks a tower becomes so filled with carbon that it ceases to work. It is then blown out with inert gas (carbon dioxide), and a current of air is passed through. This completely burns the carbon, which is swept away as carbon dioxide, and converts the nickel to oxide. The tower is then again swept out with carbon dioxide to displace the air, and put into operation again. The coal-gas first reduces the oxide to nickel and this is as active as before in the removal of the carbon disulphide," p. 1368.

While the book is very interesting as a whole, there are several places which are not up to standard. The paragraphs under photography, p. 502, on the latent image might have been written years ago. The colors of colloidal gold are not due primarily to differences in the forms of the particles, p. 524; they are due to differences in the size of the particles. It seems a pity to use the word glucinum instead of beryllium, p. 637. It is true that there are definite chemical compounds, Cu_3Sn and Cu_4Sn; but it is not true that there is no liquation when melts of these compositions are cooled, p. 880. It is misleading to say, p. 1056, that "Weiser considers that an indefinite number of hydrous oxides [of chromium] exist," because Weiser was not speaking of definite chemical compounds, though that is what one would suppose from the context.

The authors cannot bear to give up the chromites, p. 1058. "Although the solubility of chromic hydroxide in aqueous alkalis is doubtless due largely to the action of the alkali in converting the gel into a true colloidal solution, it must depend in part on the fact that, like alumina, chromic oxide acts as an acidic oxide towards strong bases, yielding salts like the chromites."

It shows confusion of mind, p. 1217, to follow Lambert's lead and to call his very pure iron passive merely because it does not corrode readily, p. 1217. For over a century passive iron has meant something quite different and it does not simplify matters to call two entirely different phenomena by the same name.

There are surprisingly few misprints.

Wilder D. Bancroft

A Dictionary of Applied Physics. *Edited by Sir Richard Glazebrook. Vol. III. 23×17 cm; pp. vi+839. New York and London: The Macmillan Company, 1923. Price: $15.00 per volume.* This volume is devoted to meteorology, metrology, and measuring apparatus, and the subject matter is arranged alphabetically, as in the preceding volumes. Among the interesting headings are: investigation of the upper air; alcoholometry; physics of the atmosphere; thermodynamics of the atmosphere; atmospheric electricity; balances; barometers and manometers; calculating machines; clocks and time-keeping; comparators; draughting devices; mean density of the earth; earthquakes and earthquake waves; gauges; gravity survey; humidity; hydrometers; design of scientific instruments; mechanical methods of integration; latitude, longitude, and azimuth by observation in the field; line standards of length; map projections; meteorological instruments; meteorological optics; meters; metrology; nomography; combination of observations; physical oceanography; quartz fibres; radiant heat and its spectrum distribution; radiation; radio-micrometer; saccharometry; seismometry; surveying tapes and wires; tides and tide prediction; trigonometrical heights and terrestrial atmospheric refraction; measurements of volume; rating of watches and chronometers; weighing machines.

Credit for the inception of the present methods of studying the conditions prevailing in the free atmosphere is given to Lawrence Rotch, p. 1, though they spell his first name wrongly.

"Norwegian meteorologists are at present engaged on the development of what promises to be a very fruitful line of attack upon the problem of forecasting. They regard the weather of the northern hemisphere as largely dependent upon the existence of a surface of discontinuity between polar and equatorial air. Helmholtz showed that such a surface of discontinuity should tend to form, and Professor Bjerknes and his associates claim that it can be detected at the earth's surface as a line of discontinuity in atmospheric conditions. The polar air is cold, dry, and transparent, often moving from an easterly point, and the equatorial air warm, moist, with poor visibility, always blowing from a westerly point. The line of discontinuity which is called the 'polar front' passes through the centres of cyclones, connecting the centre of one cyclone with those of the preceding and following cyclones. The part from the centre to the front margin of the cyclone is called the steering surface or 'anaphalanx,' and the part from the centre to the rear margin the squall surface or 'kataphalanx'. All the weather incidental to the passage of the depression is referred to the anaphalanx and kataphalanx." p. 40.

"At present the investigations of the Norwegian meteorologists are incomplete, and no judgment is possible as to the final value of their ideas, so far as application to the weather of the British Isles is concerned. It is a practical problem to trace the polar front in the whole of its course round the globe, and a network of observers will be required to keep track of its changes from day to day. It remains to be seen whether a cyclone is to be accounted for as an almost stationary wave in the polar front. This would appear to require that the axis of the cyclone should always be inclined in a northerly direction," p. 41.

Simpson's theory of the thunderstorm seems to be accepted as the most probable, p. 43. The chief objection to it is not stated, namely that there is no certainty that the positively charged drops will coalesce after being carried up. It would seem to the layman that these drops would repel each other long before a sufficient charge was built up to produce lightning.

"Photographs of lightning taken with a rotating camera show that it consists mainly of unidirectional discharges. The path of the discharge is built up piecemeal by progressive ionisation, beginning with a small branching spark, followed in a small fraction of a second by another which is somewhat longer, and the process continues until the main line of the discharge is built up. A photograph of a flash of lightning bears a close resemblance to a map showing a river and its tributaries. The accumulation of a large amount of electricity in a small space which is incidental to the passage of lightning produces, a strong repulsion of electrified particles, so that a compression wave of air of explosive violence is produced, followed by a wave of rarefaction, succeeded by waves of less intensity. W. Schmidt showed that only a very small part of this energy takes the form of audible waves, so that we hear only a very small part of thunder. It may be noted that lightning affects wireless apparatus, and a directional wireless set can be adapted to detection of thunderstorms. By the use of a number of directional stations it has been found possible to follow the course of thunderstorms for long distances," p. 43.

The figures in regard to rain from water vaopr are quite impressive, p. 45. "A cube of air ten metres in the side weighs about 1.25 metric tons. In summer on the average in this country it would contain ten kilogrammes of water-vapour, and would supply water enough to cover the base of the cube with rain to the depth of 0.1 mm. All the water except 0.03 gramme per cubic metre could be extracted by reducing the temperature to 222°

Abs., by elevating it to about 11000 metres, where the pressure would be about 232 millibars; hence, confining attention to a limited area, a fall of rain of one millimetre would correspond with the desiccation of a column of air 100 metres high and no more. We have to consider whether such a process may be regarded as natural.

"One millimetre of rainfall over a square kilometre represents a million kilogrammes or a thousand metric tons. The dynamical equivalent of the thermal energy set free by the condensation of water to the extent of a millimetre of rainfall over a square kilometre is 6×10^{11} thermal units or 2.5×10^{12} joules, about a million horse-power-hours. And as the practical unit of area for the fall of rain may be regarded as a hundred kilometres square, the energy with which we have to deal in the ordinary way is of the order of ten thousand million horse-power-hours. It must be remembered that when rainfall is produced, energy to the corresponding extent must be disposed of. It is not uncommon to find suggestions that air may be 'supersaturated' before rainfall. There is no evidence in support of the view, but even if it were true the disposal of the energy is not avoided; it must have taken place in order to produce the supersaturated air."

Producing rainfall from a clear sky is therefore a stupendous task. The writer of the article, Sir Napier Shaw, has not mentioned however that most rain comes from clouds and that the equivalent of all this vast expenditure of power has been expended in producing the cloud. The amount of work to be done on a cloud to produce rain may be negligible because the cloud is theoretically an instable system.

"A thunder-cloud may be regarded as an electric machine, by the action of which a vertical separation of positive and negative electricity is produced. It is thus essentially bipolar, equal and opposite charges being separated in the upper and lower parts of the cloud in a given time. The charges of the two poles of the cloud are, however, not likely to remain equal, on account of differences in their rates of dissipation. We may form some estimate of a lower limit to the magnitude of the charges which may accumulate in thunder-clouds by assuming that it is not less than the average quantity discharged in a lightning flash—about 20 coulombs. The potentials within the charged portions of thunder-clouds probably reach magnitudes of the order 10^9 volts. An estimation of the rate of separation of the charges in a thunder-cloud, *i.e.* of the vertical current through the cloud, may be derived from the rate at which the electric field destroyed by a lightning flash is regenerated. This method gives a few amperes as the probable order of the vertical current through a thunder-cloud," p. 85

Under atmospheric electricity we read, p. 92, that "even in calm weather and with a clear atmosphere there are minor fluctuations in the records of potential gradient superimposed upon the regular periodic variations. Clouds other than rain clouds do not as a rule produce changes which are large compared with the normal potential gradient. Within a fog, however, the potential gradient generally rises to several times its normal value.

"Clouds of dust raised by the wind may produce changes in the potential gradient, the sign of the effect depending on the nature of the dust. Drifting snow at low temperature—as has been found in all the recent Antarctic expeditions—has very large effects, generally giving very high positive potentials. According to Simpson, the effects of drifting snow may be explained by supposing that when ice crystals strike one another in air the air becomes positively charged, the ice negatively."

Under balances we find that "lacquer, if used as a protective coating for a weight, should be hard, of moderate thickness, smooth, and not likely to chip. It is well known that lacquers absorb moisture from the air to a variable extent, say from 1 to 5 percent of the weight of the lacquer, depending on the atmospheric humidity. On an estimate, a 100 grm. lacquered weight may be subject to variations of the order 0.0001 gramme. This value is, of course, only approximate, since much depends on the nature and the method of application of the lacquer. Nitro-cellulose lacquers have been found to absorb about three times as much moisture as those containing shellac. The use of a lacquered weight would probably preclude an accuracy exceeding 0.0001 gramme on 100 grammes, whereas an uncoated polished brass weight would in general maintain a rather better consistency of mass than this for a period of several months, under good conditions of use," p. 123.

"When the air very close to the ground is much heated it may happen that rays of light can pass into this lowest layer and curve upwards again. In such circumstances an observer will receive the same impression as if the rays had been reflected from the surface of water; when he can thus see an object and its inverted image he is said to observe a mirage; that term is used somewhat loosely, however, for other kindred phenomena. The illusion of the presence of water is frequent, but it does not always occur. . . .

"When the sheet of water is apparently present its near edge will be determined by rays which almost graze the ground. The illusion of reeds growing by the water-side is produced by the vertical extension of the images of pebbles which happen to be suitably placed.

"It has been mentioned that a rapid increase of air density from below upwards leads to a narrowing of the horizon; the horizon in this sense is really identical with the near edge of the sheet of 'water', but it may happen that it does look like the ordinary horizon, and in such circumstances an object beyond the 'horizon' and its reflection or mirage may be merged and seen to float in the air.

"Though typical of tropical deserts, mirage is not infrequently to be observed in England. Excellent examples have been seen on level wood pavement in the London suburbs, wide roads appearing to be completely flooded.

"The same type of mirage can occur at sea; much more frequently it happens that, when a distant coast is looked at, a bright whitish strip is seen along the sea-horizon in front of the coast. To the casual observer the strip seems to be the actual shore. In this case the mirage or reflection of the land is of little depth and is not noticeable, the bright strip is the reflection of the sky. The phenomenon is an indication that the sea is warmer than the air above it," p. 520.

"Another type of mirage is that in which the reflecting layer is above the observer. The necessary condition is an exaggerated falling off of air density at a certain height, implying a sharp 'inversion' or increase of temperature with height. In this case the object is seen inverted, and frequently there is an erect image above the inverted one, indicating that three alternative routes are available for the light from object to observer. The most striking examples of the phenomenon have been reported from the Arctic regions; on one occasion a ship twenty-eight miles away, and therefore far below the horizon, was seen reversed in the air and actually recognised. . . .

"Fata Morgana is the Italian name for Morgan the Fairy, the legendary half-sister of King Arthur. The mirage seen across the Straits of Messina suggested the poetical palaces in the fairyland where Fata Morgana reigned, and her name is now given to mirages seen in like situations where there is much distortion and repetition of images. In such cases superior and inferior mirages may be produced simultaneously by interlacing currents of air," p. 521.

"Patches of colour like mother-of-pearl are occasionally seen on high clouds such as cirro-stratus. These patches are probably portions of coronas of very large radius. The classical explanation attributes them to diffraction by ice-needles. The complete theory of diffraction by a cloud of needles with fortuitous orientation does not seem to have been worked out, but it is improbable that sufficiently brilliant colours could be produced by such a cloud. Simpson prefers to attribute the phenomenon to minute water-drops, supporting this view by his observation that a corona and a halo are never seen at the same time on the same cloud. There is abundant evidence for the existence of drops at temperatures far below the freezing-point," p. 527.

"The larger number of observations on the transparency of sea-water have been made by noting the maximum depth at which a white disc, generally 0.5 m. in diameter, can be seen. The depth obviously depends to a large extent on the altitude of the sun and the amount of disturbance of the surface, so that the results are only roughly quantitative. The maximum depth recorded is 66 m. in the Sargasso Sea, with a disc 2 m. in diameter. In the North Sea the depth varies from 5 to 12 m. in the southern part to 20 m. or more northwards of the Dogger Bank, in the open oceans 50 to 60 m. has been often recorded," p. 672.

"Oxygen and nitrogen (including argon) are absorbed according to their solubility under the particular conditions of temperature and partial pressure, while the solubility of carbon dioxide is affected by the fact that it is in equilibrium with dissolved carbonates. It has often been suggested that the amount of dissolved gases in an under-current could be used to determine where it was last at the surface. In the case of oxygen this is incorrect, experiment has shown that there are great bodies of water very deficient in oxygen, which must have been removed by living organisms. Nitrogen might give better results but great uncertainties are caused by the mixing of the under layers," p. 673.

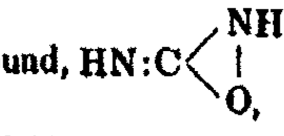
"The use for which quartz fibres are almost exclusively required is as torsion fibres in delicate apparatus, and for this purpose they are pre-eminent. With diminution of diameter the cross-section varies as the square of the diameter, and the strength falls off less rapidly than this. On the other hand, the torsional rigidity falls in the proportion of the fourth power of the diameter or square of the sectional area. For some classes of experiment, therefore, the angular deflection will become greater as the scale of the apparatus is reduced, and the consequent increasing delicacy is limited only by the difficulties of manipulation, construction, or measurement, or by relatively increasing effects of disturbance, if such is the fact, and last by the viscosity of the air. With any but the simplest form of suspension the resistance to motion due to this cause may be such as to pass the dead-beat conditions, in which case deflections require an inordinate time, or if within the dead-beat conditions by too small an amount the determination of period is made difficult on account of the high logarithmic decrement. The easiest way to attach a quartz fibre at its ends is to use pointed wires wetted with shellac varnish, and lay the end of the fibre on the varnish, and then gently pull in the direction of the point so that the fibre lies in this direction at the point. Then on drying, with or without the aid of heat, the fibre will be held. Where there is any question as to the rigidity of such a fastening, other methods may be used. A solution of silicate of soda has been used successfully, but the writer has no experience with this. Cements of the 'Caementium' type would no doubt answer very well, but the writer used in his experiments on the constant of gravitation a very secure and rigid method of fastening, effected by silvering electro-coppering, and soldering the coppered ends to metal tags of enormous area relatively, and cementing these tags," p. 697.

"All fibres seem to show increasing tenacity with diminution, as though there were a surface tenacity akin to surface tension in liquids and the great strength of silk and spider lines is no doubt due to this cause. Such strength in fine quartz fibres is not due to the fact that the surface is a natural or vitreous surface resulting from fusion, for if a coarser fibre is made to carry a weight over a pail of water, and then a sponge dipped in hydrofluoric acid is placed against the fibre so as to dissolve it slowly—it is very slow compared to glass—the fibre will break when it is reduced sufficiently in diameter, and the one end will immediately be washed in the water. The diameter is then found to be the same as that of a whole fibre which is just broken by the same weight. Tenacities up to from 60 to 80 tons to the square inch, to use the engineer's units for comparison, with metals, are found with fibres 1/7500 inch or 1/300 millimetre in diameter or less," p. 698.

On p. 717 the conclusion is drawn that "the sun's effective radiating layer is roughly comparable with that of a black body at about 6000°K or about 5700° C."

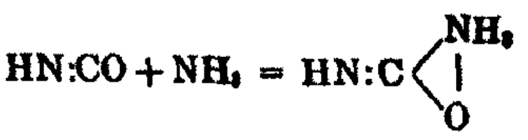
"As an illustration of the accuracy of the predictions made with the Indian tide-predicting machine, the following comparisons of observed and predicted times and heights for Prince's Dock for the year 1917, furnished by the Indian Survey Department, may be taken. High-water times: 43 percent within 5 minutes, 82 percent with 15 mins., 97 percent within half an hour. With regard to the few occasions on which the difference exceeds half an hour, it may be remarked that where the diurnal components are large the whole amount of rise and fall at neap tides may often be very small and the changes in level at high and low water therefore very small. At a number of ports, *e.g.* Aden, often only one high and one low water occur in the 24 hours at neaps. High-water heights: 63 percent within 4 inches, 92 percent within 8 inches, 100 percent within 1 foot; only a very few differences exceeded 1 foot. The spring range at Prince's Dock is about 14 feet," p. 765.

Wilder D. Bancroft

The Chemistry of Urea. *By Emil A. Werner. 26×16 cm; pp. x+212. London and New York: Longmans, Green and Co., 1923. Price: $4.75.* The author's thesis is that urea is a cyclic compound,  $\mathrm{HN{:}C}\left\langle\begin{matrix}\mathrm{NH_2}\\ |\\ \mathrm{O}\end{matrix}\right.$, and not carbamide, while urea hydrochloride is $\mathrm{HN{:}C(OH)NH_3Cl}$. Wöhler's synthesis of urea from ammonium cyanate is believed to take place in three stages, p. 13: the dissociation of ammonium cyanate giving ammonia and cyanic acid in the enol form, $\mathrm{HOC{\vdots}N}$; the change of cyanate acid from the enol to the keto form, $\mathrm{HN{:}C{:}O}$, as an effort to attain greater stability; and the reunion of ammonia with cyanic acid in the altered form to produce urea of constitution quite different from carbamide. Cyamelide is the polymerization product of the enol form of cyanic acid and cyanuric acid the polymerization product of the keto form. When cyanic acid polymerizes spontaneously at 0°, the product is about sixty percent cyamelide white it is entirely cyanuric acid when the change takes place at a high temperature, as during the decomposition of urea by heat, p. 17.

The formation of urea during the hydrolysis of cyanic acid at 0° has been proved by Werner and Fearon, p. 19. "Not less than six consecutive changes are involved when cyanic acid is decomposed in the presence of water. These are conveniently divided into two groups:—

Primary changes

(1) $\mathrm{(HOCN \rightleftarrows HNCO) + H_2O = CO_2 + NH_3}$
(2) $\mathrm{HOCN + NH_3 = NH_4OCN}$
(3) 

$$\mathrm{HN{:}CO + NH_3 = HN{:}C}\left\langle\begin{matrix}\mathrm{NH_2}\\ |\\ \mathrm{O}\end{matrix}\right.$$

Secondary changes

(4) $\mathrm{NH_3 + CO_2 + H_2O = NH_4HCO_3}$
(5) Interaction of urea and HNCO = biuret
(6) Production of cyamelide.

"In an aqueous solution of cyanic acid at 0°, and at concentration approximately N/4, the primary changes are completed in from seventy-five to ninety minutes, and under such conditions the secondary changes, with the exception of No. (5) are completely suppressed up to the point at which the primary ones are just completed."

The author makes a statement on p. 16 which is true for other things besides urea. "The whole chemistry of urea abounds in secondary reactions, nearly all of which have been lightly passed over as of no consequence so far as the main reaction is concerned. Secondary reactions are almost invariably the beacons which light up the path to the proper understanding of the mechanism of the main reaction. Failure to appreciate this fact has been largely responsible for the many erroneous interpretations of the decompositions and reactions of urea."

When studying the pressure-concentration relations of vaporized urea, Isambert drew the conclusions that solid carbamide may be regarded as formed by a simple addition of carbonic acid and ammonia gas, and that the volatilization of urea is therefore a phenomenon of dissociation, p. 30. "Whilst the latter remark is quite true, it is evident that, taken in conjunction with the former, Isambert has completely ignored the existence of the vapour of cyanic acid as a product of the dissociation of urea. In these experiments urea was vapourised at 61°-62° under a much reduced pressure. Since the molecular weights of cyanic acid and of carbon dioxide are as 43 to 44, a mixture of the vapour of the former and ammonia would be likely to behave as Isambert found. . . .

"Proof of the direct association of urea into ammonia and cyanic acid has been supplied by Escales and Köpke (1911), who showed that when urea was sublimed in a vacuum at 160°, the sublimate was ammonium cyanate. Their remark that, if Wöhler had sought to purify his synthetical urea by sublimation in this way, his famous discovery might never have been made, is one with which the writer is by no means prepared to agree. Wöhler was much too shrewd and careful an observer to overlook the properties of a substance so different from ammonium cyanate. Had not his own observations on the subject discussed in the present chapter been overlooked by many others, much unnecessary work might have been spared."

"The text-books have been unanimous in stating that urea is decomposed in a normal manner by nitrous acid like all other amides, the simple equation

$$(3)\ CON_2H_4+2HNO_2 = CO_2+2N_2+3H_2O$$

being given as the correct expression for the change.

"Theoretically, this reaction should be available for the estimation of urea, on the basis of the volume of nitrogen evolved, and indeed this is commonly suggested for the literature. It is never used for this purpose, and it never has been, since experiment has proved it to be quite valueless. On the other hand, it constitutes a well-known method for the estimation of nitrous acid, with a very fair degree of accuracy, on the supposition that the above equation is true. It was no doubt for this reason, and on account of the employment of other methods for the estimation of urea, that this reaction was not considered deserving of any further investigation.

"A careful quantitative study of the behaviour of urea towards nitrous acid was made by the writer in 1917. The results have supplied convincing evidence in support of the cyclic formula of urea.

"The following facts were clearly established:—

"1. Urea and pure nitrous acid in aqueous solution do not interact.

"2. The presence of a strong acid (hydrochloric, or nitric) quickly promotes a brisk interaction, even in dilute solutions, and the reaction is then completed in a relatively short time.

"3. The presence of a weak acid, such as acetic acid, does not promote an interaction, unless the concentration is abnormally high, and even then the velocity of the reaction is extremely slow.

"4. The volume of nitrogen evolved is not a direct measure of the amount of urea decomposed, calculated on the basis of equation (3); the quantity decomposed is much greater than that indicated by the evolved nitrogen.

"5. Only when urea is present in considerable excess is the volume of nitrogen evolved an approximately true estimate of the amount of nitrous acid decomposed.

"6. The volume ratio of carbon dioxide to nitrogen (1:2) required by the equation is never obtained; the proportion of carbon dioxide is always much higher; moreover, the composition of the gas is liable to much variation with small changes in concentration.

"It is obvious that, so far as the usual explanation of this reaction is concerned, all these facts stand out as anomalies for which the ordinary equation offers no explanation. Now, anomalies in such a reaction can have no reality; their apparent existence is the natural consequence of an erroneous conception of the change, and when the true constitution of urea is considered they appear as normal phenomena which reveal the true mechanism of the interaction," p. 49.

When urea (in the form of a salt) and nitrous acid interact, a certain proportion of nitrogen from the urea is always fixed, as an ammonium salt, and herein lies the fallacy of the reaction, so far as the estimation of urea is concerned.

"The variations observed in the ratios of carbon dioxide to nitrogen are thus easily explained, since the volume of nitrogen evolved is lowered in proportion to the amount of cyanic acid hydrolysed. The latter change can be only partly suppressed, even under the most favourable conditions (that is, high concentration and nitrous acid in excess), with the result that the ratio of carbon dioxide to nitrogen evolved is never that which has been erroneously assumed.

"Now, according to the above explanation, the interaction of urea and nitrous acid is theoretically clearly divisible into two stages, during the first of which one molecule of urea is completely decomposed by one molecule of nitrous acid, instead of by two molecules, as has been commonly, but falsely, supposed.

"This has been easily proved experimentally, by adopting the exact conditions which the theory rigorously demands, namely, (1) the presence of urea in excess at the outset, (2) a low concentration of nitrous acid, (3) the presence of mineral acid in excess of that required to neutralise ammonia generated from the hydrolysis of cyanic acid and so to maintain the proper configuration of the urea molecule. Under these conditions the decomposition of cyanic acid by nitrous acid can be almost completely suppressed in favour of its decomposition by hydrolysis," p. 52.

"In order to prove that urea is not attacked by pure nitrous acid alone, it is necessary that the concentration of the latter should not be greater than N/30. Under such condition, the solution being protected from the light which promotes decomposition of nitrous acid, no interaction was found to take place even after three days; yet on the addition of two drops of hydrochloric acid solution a brisk reaction was quickly promoted, and even at this low concentration of nitrous acid was almost completed at the end of half an hour," p. 56.

"Mixter (1882) obtained urea by passing carbon dioxide and ammonia through a tube heated to low redness. There can be no doubt that cyanic acid was generated in this case, thus—

$$CO_2+NH_3 = HN{:}CO+H_2O,$$

as Mixter has suggested. It was shown by the writer (1920) that when ammonium carbamate was vaporised through a glass tube heated to incipient redness, ammonium cyanate and urea were found in small quantity in the cooled product," p. 66.

"Fichter, Stutz and Grieshaber (1912) and Fichter, Steiger, and Stanisch (1918) showed that when a concentrated solution of ammonium carbamate was electrolysed with a direct current, a small quantity of urea was formed exclusively at the anode," p. 70.

"Since urea was formed only at the anode in Fichter's experiments, there can be no doubt that the formation of cyanic acid by oxidation is the pre-final step in this synthesis. Indeed Fichter has himself supplied evidence in support of this conclusion. Urea was obtained by electrolysing a solution of ammonium acetate containing methyl alcohol. The latter, it is stated, gives carbon monoxide, and the change was represented thus—

$$CH_3OH \longrightarrow CO \longrightarrow H\cdot CO\cdot NH_2 \longrightarrow H_2N\cdot CO\cdot NH_2.$$

"Formamide, which was assumed to be produced (apparently by union of CO and NH_3), was oxidised to urea in the presence of ammonia.

"The obvious explanation of the change is

$$CO+NH_3O = HN{:}CO+H_2O.$$

"The fact that the formation of urea is promoted in all these reactions by the presence of free ammonia is easily understood, since the latter is necessary to 'fix' the cyanic acid produced. The formation of urea from ammonium carbamate furnishes a striking illustration of the difficulties which have been encountered in attempting to explain a simple phenomenon, solely as the result of the belief in the 'carbamide' formula," p. 70.

"We have now to consider an interesting synthesis of urea, in which the compound is certainly not formed from the interaction of cyanic acid and ammonia. In 1851 Cannizzaro and Clöez showed that when a small quantity of nitric acid was added to a solution of cyanamide in ether, crystals of nitrate of urea gradually separated. Baumann (1873) obtained urea (originally as sulphate) by adding cyanamide to a 50 percent aqueous solution of sulphic acid. He pointed out that very concentrated acid was necessary to obtain urea from cyanamide, and whilst more or less dicyanodiamidine ($C_2H_6N_4O$), or so-called guanyl-urea, was always formed, the proportion of the latter increased with the dilution of the acid. Drechsel (1880) prepared the compound $CN\cdot NH_2, 2HCl$, by passing dry hydrogen chloride into a solution of cyanamide in anhydrous ether, and proved that when decomposed by water it did not afford urea, but only dicyanodiamidine.

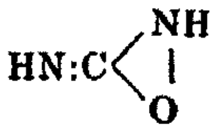
"No investigator, so far as the writer is aware, has ever yet claimed to have obtained urea by heating cyanamide either with water alone, or with an aqueous alkaline solution. In fact 'free' urea has never been directly obtained by the hydrolysis of cyanamide under any condition.

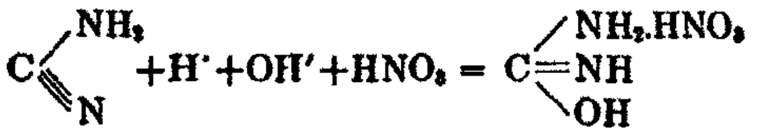
"Nevertheless the simple equation

$$CN\cdot NH_2+H_2O = H_2N\cdot CO\cdot NH_2$$

has been universally adopted to represent the production of urea from cyanamide, as if the reaction was one which proceeded on perfectly normal lines. The change, accepted in the above form, has always been put forward to support the 'carbamide' formula, on the supposition that cyanamide is related to urea as a nitrile to an amide.

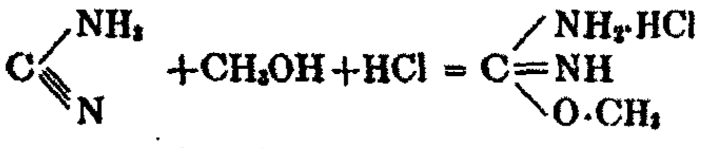
"Now nitriles are readily hydrolysed to their related amides, when heated with either dilute acids or alkalis, or even with water alone in most cases. It is evident, therefore, that the very special conditions necessary to hydrolyse cyanamide to urea (as a salt) appear anomalous in the light of the above simple relationship. The true mechanism of the change only becomes intelligible when due consideration is given to the constitution of cyanamide, and to the fact that the structure of the urea molecule in the free state is not the same as when present in the form of a salt," p. 80.

"A comparison of the cyclic formula  $HN{:}C\langle{}^{NH_2}_{O}$ with either of the two formulae of cyanamide shows that the relation of urea to the latter is not the simple one which has been hitherto supposed. The conditions under which urea can be formed show that cyanamide must assume the amino form before hydrolysis, and since the ions H and OH_1 are undoubtedly the active agents which take part in the change, this may be represented by the following equation:—



$$C\begin{matrix}\diagup NH_2\\ \equiv N\end{matrix} +H^{\cdot}+OH'+HNO_3 = C\begin{matrix}\diagup NH_2.HNO_3\\ =NH\\ \diagdown OH\end{matrix}$$

"This reaction, which is analogus to the formation of 'isoureas' from cyanamide and alcohols in the presence of hydrogen chloride, thus—



$$C\begin{matrix}\diagup NH_2\\ \equiv N\end{matrix} +CH_3OH+HCl = C\begin{matrix}\diagup NH_2\cdot HCl\\ =NH\\ \diagdown O\cdot CH_3\end{matrix}$$

shows that urea, when generated, has the 'isourea' structure, which is retained only in the salt, and in the presence of a small quantity of water," p. 87.

"The special conditions necessary for the production of cyanamide from urea are in perfect agreement with the writer's theory of the constitution of the latter in the free state and in the form of a salt. As cyanamide can be hydrolysed only to a salt of urea, so from a salt of urea only can it be regenerated," p. 93.

The mechanism of the decomposition of urea by urease is explained by Fearon, thus, p. 110: "urease condenses urea by adsorption on its surface; this is followed by the dissociation of the urea into ammonia which combines with the enzyme, and cyanic acid which is hydrolysed by the solvent, in the case of water. . . .

"Apart from any theory of the mode of action of the enzyme in the first step of the change, the outstanding result of Fearon's researches proves that urease is not directly concerned in the 'hydrolysis' of urea at all. The function of the enzyme is to bring about the dissociation of urea into ammonia and cyanic acid. The hydrolysis of the latter follows as a secondary change in the presence of water.

"The theory that urease acts as a dissociating agent in attacking urea offers a new conception of enzyme action which it is not unlikely may be applied to other cases. We have in this theory a rational explanation of the specific action of urease. It was pointed out that methyl and ethyl-ureas requre a higher temperature than urea for their dissociation and hence the velocity of their 'hydrolysis' when heated in the presence of acids and alkalis respectively is much slower than in the case of urea. Now, no enzyme has been found to exert its activity above 80°, whilst many are inactive at about 70°; hence if the enzyme cannot bring about the dissociation of a substituted urea below 80°, say, the latter cannot be 'hydrolysed'. Fearon (1921) has shown that whilst methylurea is not attacked by soy bean urease up to the limit temperature, ethylurea is attacked slowly by the enzyme at 70°.

This is an interesting fact in support of the new theory, since it appears to indicate that urease is capable of bringing about the dissociation of ethylurea—less stable than methylurea—just below the temperature limit of its activity.

"Quite recently Fearon has found that pure normal butylurea is attacked by soy bean urease at 45°-50°. Now this is a point of further interest, since this urea, being less stable than ethylurea, is dissociated at a lower temperature, and hence is attacked by the enzyme at a temperature below that at which it can decompose the ethyl derivative.

"The possibility of effecting a synthesis of urea by urease from ammonium carbonate, as a result of a direct dehydration of the latter, as claimed by Barendrecht (1919-20), appears more remote than ever in the light of the 'dissociation' theory.

"The decomposition of urea by urease is another example of a reaction in the chemistry of urea, the interpretation of which has been greatly helped by a recognition of the cyclic formula."

Up to comparatively recent years urea was considered to be a product peculiar to animal metabolism; but the author ventures now, p. 120, "to make the sweeping assertion that urea is a constant product of the breaking down of vegetable protein during the germination of all seeds.

"As Fosse has pointed out, the plant can be the seat of the two inverse phenomena of formation and destruction of urea. This condition, in all probability, can only obtain in young plants, since the function of urease is to destroy urea produced from proteins as the result of hydrolysis and oxidation. We can understand why certain leguminous seeds, so rich in protein, should also be rich in urease. Those seeds which, in the dormant state, do not happen to contain the enzyme ready formed, produce it, no doubt, in quantity during the process of germination.

"Urease in its relation to vegetable protein is therefore comparable to zymase in its relation to starch. Whilst the latter enzyme is the active agent in the final breaking down of starch into the simple products alcohol and carbon dioxide, urease is the active agent in the corresponding resolution of protein into the simple products cyanic acid and carbon dioxide. The ultimate oxidation of alcohol to carbonic acid and water, from which the plant originally prepared the starch, and the hydrolysis of cyanic acid to carbonic acid and ammonia, from which the protein was originally prepared, these are changes with which the enzymes are not directly concerned."

"In all cases where the formation of urea has been shown by the oxidation of protein matter, of an amino-acid, or of a carbohydrate in the presence of ammonia, Fosse (1919, 1921) has demonstrated that cyanic acid is the precursor of the urea. Whilst the writer is not prepared to accept the theory of the formation of cyanic acid which has been put forward by Fosse (1919), which involves the intermediate production of hydrocyanic acid, the main point is the recognition of cyanic acid in all these oxidation changes.

"It is obvious, as Fosse pointed out, that the urea molecule cannot participate in nitrogenous nutrition without suffering a preliminary decomposition, which is assumed to be the production of ammonia and carbonic acid by the action of urease. We know now from Fearon's work that the action of the enzyme is limited to the production of ammonia and cyanic acid. If the latter, as suggested by the writer, is directly concerned in the building up of proteins, then its hydrolysis in the plant cells is a superfluous change. Interesting evidence in support of this view was given by the experiments carried out many years ago by Ville (1862). He showed that urea acted as a powerful stimulant to vegetation on plants grown in an artificial soil of sand. Urea was more efficacious than carbonate of ammonia, and its favourable results were manifested with great rapidity.

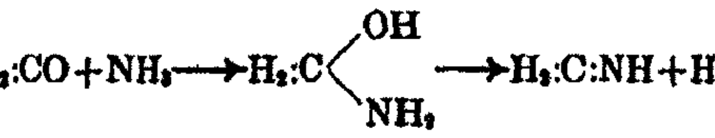
"With ethylurea the results were very different: the growth was checked, the plants drooped and were stunted, the effect being the same as if the sand had not received the addition of any nitrogeneous material. The experiments were repeated a great number of times over a period of two years. The results did not vary.

"Seeds were found to germinate in the ordinary manner in the presence of ethylurea, but as soon as the young plants put forth their first leaves, the extremities of these became white and shrivelled, and the effect gradually spread over the rest of the leaf. The changes during germination being independent of the presence of an outside source of nitrogen, growth proceeded for a short time on normal lines," p. 121.

"The absence of an enzyme capable of decomposing ethyurea *at the ordinary temperature* into ethylamine and cyanic acid explains Ville's results in the light of modern investigations. Whilst the superior effect of urea, as compared with a simple salt of ammonia, in promoting vegetation is to be ascribed to its power of immediately supplying cyanic acid, the subsequent production of the latter from the ammonia generated at the same time requires consideration.

"The formation of cyanic acid by the oxidation of ammonia in the presence of carbohydrates is no doubt a slower reaction, *at ordinary temperature*, than the decomposition of urea by urease.

"Formaldehyde being the first product of carbon assimilation, the above change may be assumed to proceed on the following lines:—

(1) 

$$H_2{:}CO+NH_3 \longrightarrow H_2{:}C\begin{matrix} OH \\ NH_2 \end{matrix} \longrightarrow H_2{:}C{:}NH+H_2O$$

$$(2)\ H_2{:}C{:}NH+O_2 = O{:}C{:}NH+H_2O$$

"It is probable that reaction (2) is brought about by the 'catalytic' effect of one or other of the different types of enzymes collectively classed as 'oxidases", and which are so widely distributed in plant cells. According to the theory presented here, it follows that so far as assimilation of nitrogen from ammonia is concerned, the phenomenon is inseparably connected with carbon assimilation.

"Takabayashi (1897) found that 0.50 percent solutions of carbonate of ammonia had an injurious effect on certain plants, such as barley, wheat, and onions, but this was counteracted by supplying the plants with cane-sugar or with glycerol. Experiments with other ammonium salts confirmed their injurious effect in the absence of sufficient sugar in the plant.

"Since the function of the plant is to build up protein from urea, or from any other source of nitrogen available, it seems highly probable that the 'formation' of urea in developed plants is accidental rather than intentional. Its occurrence is, in the writer's opinion, strong evidence of the production of cyanic acid as a first step in protein building," p. 122.

"Whilst the 'cyanic-acid-precursor' theory of the formation of urea does not preclude the formation of ammonia in the body from a source other than the hydrolysis of cyanic acid, it seems very probable that much of it (perhaps all) originates in this way," p. 130.

"The dehydration of ammonium carbonate or carbamate—it does not matter which—has been the favorite theory of the origin of urea. Since ammonium carbonate is not normally present in urine, urea must be assumed to be formed quantitatively from it by dehydration at the low temperature of 36°-37°. Now, in order to imitate this seemingly simple change *in vitro*, a high temperature and a high pressure are necessary, and even then the yield of urea is small. If the mechanism of the change is the same *in viva* and *in vitro*, we have no explanation for this difference. When the true origin of the formation of urea *in viva* is brought to light, we find no difference in the conditions under which the change can be effected outside the body, for the simple reason that the formation of natural and of artificial urea in the free state is similar in mechanism.

"Most of the chemical changes taking place in plants and in animals are effected through the agency of enzymes. It is interesting to note that in every case where an enzyme, or the preparation containing the active elements which we call an enzyme, responsible for any definite chemical change has been isolated from its natural source, it is found to reproduce the particular change *in vitro* under conditions no different as regard temperature, pressure, and nature of solvent, and on the same lines as in the living organism," p. 131.

"The reciprocal action of animal and plant life in relation to carbonic acid and carbon assimilation is well recognised. From carbon dioxide and water plants build up complex carbohydrates from which animals derive energy in oxidising them to the two simple substances from which they were formed. Similarly, plants absorb ammonia, which is oxidised in the presence of carbohydrates to cyanic acid, which is used in the building up of protein matter. Animals, by hydrolytic and oxidation changes, break down proteins to cyanic acid and ammonia, which are excreted as urea, from which plants again derive the necessary material to continue the cycle of changes," p. 132.

"When HCl combines with NH_3, the constitution of the product must not, in the writer's opinion, be considered solely from the point of view of the valency of the nitrogen atom. Whilst the valency of the latter is assumed to be raised from three to four, the valency of chlorine is simultaneously raised from one to two—a co-valent effect in fact. The constitution of the salt may be represented by the expression

$H_3\underline{\pm}N\underline{\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;}\overset{-}{Cl}\text{-}H$," p. 160.

"It does not appear to be generally recognised that alkalinity of the solution is essential in order that urea may be decomposed by either a hypochlorite or a hypobromite. In a neutral, or even faintly alkaline, solution urea remains indifferent to the reagent, so far as the evolution of gas is concerned. The case is comparable to the behaviour of urea towards nitrous acid. We have seen that with the latter a change in the configuration of the urea molecule is necessary before oxidation can take place. A similar change apparently occurs before urea can be decomposed by a hypohalogenite. The excess of alkali commonly present may be assumed to bring about the required condition," p. 171.

In the last chapter, there are given sixteen experiments "selected to demonstrate the chief reactions of urea and to bring out the main facts which illustrate its properties and supply evidence of its [cyclical] constitution."

Wilder D. Bancroft

Anorganische Chemie. *By Fritz Ephraim. Second and third improved edition. 25×16 cm; pp. viii+742. Dresden and Leipzig: Theodor Steinkopff, 1923. Price: $2.00.* The subject is presented in nine chapters: the elements; the halogen compounds; the oxides of hydrogen and the metals; the compounds of sulphur, selenium, and tellurium; the nitrogen, phosphorus, and arsenic group; the fourth group of the periodic system, and boron; the rare earths; the intermetallic compounds; the radio-active elements.

There are a number of things which are either well presented or of special interest to the reviewer. In fused lithium hydride the lithium is cation and the hydrogen anion, pp. 31, 704. The author distinguishes two groups of metals, so far as alloying with hydrogen is concerned. With iron, copper, nickel, and platinum, the amount of hydrogen taken up at constant pressure increases with rising temperature, which is certainly surprising. With palladium and tantalum, the reverse is the case, p. 701. "These alloys are absolutely metallic in appearance and in them hydrogen functions exactly like a metal. Hydrogen is monatomic in these alloys, which perhaps has something to do with the increase in solubility at higher temperatures, since it is chiefly hydrogen atoms that are taken up; and it is only at higher temperatures that there are enough hydrogen ions in hydrogen gas to make a distribution ratio possible." One wonders whether monatomic, electrically neutral, hydrogen may not be metallic. The reason why solid or liquid hydrogen is not metallic may be because it is diatomic.

Eleven pages, pp. 48-59, are devoted to colloids. Graphite is not considered a definite substance, p. 84. In fact the author shares Hulett's view that carbon is really graphite. The author adopts the view of Kohlschütter that in graphite the particles are arranged into fairly regular plates, while this is not the case in carbon black. The author considers, p. 107, that in the formula for hypochlorous acid the chlorine and oxygen are both joined to the hydrogen as well as to each other. He accounts for the reducing action of ammonia and arsine by calling the dissociating compounds sources of nascent hydrogen, pp. 133, 483. Arsine, for instance, will precipitate silver from an aqueous silver nitrate solution. Phosphine, arsine, and stibnine all behave the same way with silver nitrate, giving first a yellow precipitate of unknown composition, and then metallic silver.

The reaction between hydrogen and chlorine is believed to be between hydrogen and chlorine, p. 154, and the effect of ultra-violet light is to split chlorine into atoms. Since previously illuminated chlorine reacts more rapidly than ordinary chlorine, it seems probable that exposure to light enables the chlorine to destroy negative catalysts that may be present, such as ozone, oxides of nitrogen, or traces of ammonia.

There is a six-page exposition of the phase rule, mostly in small type, pp. 165-171, a somewhat longer one, p. 222, on Werner's co-ordination theory, and a shorter one, p. 305, on the theory of oxidation, while induced reactions get half a page, p. 372, and the question of phosphorescence about the same, p. 415. The reviewer is delighted with the common-sense stand of the author. "Phosphorescence is not a characteristic of the sulphides of the alkaline earths. They do not phosphoresce when pure but the mass phosphoresces when traces are present of salts of the heavy metal, bismuth and manganese compounds, for instance. These latter determine the color of the luminescence which may be orange, yellow, green or bluish, depending on the nature of the heavy metal."

The green color of a solution containing ferrous chloride and nitric oxide is attributed to a compound formed with the anion of ferrochloride acid, $FeCl_4 \cdot 4NO'$, p. 539. The special action of aqua regia is considered due to nitrosyl chloride, p. 541. The oxidation by nitric acid in presence of nitrous acid is apparently due to nitrogen peroxide formed by the interaction of the other two, p. 547. The splitting-off of oxygen from potassium nitrate is an endothermal reaction; but the reaction between potassium nitrate, sulphur, and carbon in the form of gunpowder, is an exothermal one, p. 555. While it is shown, p. 558, that nitrous acid oxidizes hydroxylamine to nitrous oxide, it is not suggested that this is the way in which nitrous oxide is formed during the reduction of nitric acid. The author discusses the colors of arsenic sulphide to some extent; but does not take up the more important question of the colors of antimony sulphide.

"Especially characteristic of silicon is the tendency of the oxygen compounds to polymerize spontaneously. We know monomolecular carbon dioxide but not monomolecular silicon dioxide; only its polymeric forms, and the same is true of the other oxygen compounds. It is to the existence of stable, gaseous, carbon monoxide, that carbon owes most of its important part in nature. After it has undergone numberless chemical chages in plants and animals, it appears as volatile carbon dioxide, penetrating everywhere and ready to start over again making organic compounds. In the case of silicon, however, the marked tendency to form oxygen compounds leads only to 'petrifaction.' The numerous carbon compounds bear witness to the manifold responses of the carbon atom, while the natural occurrence of silicon in a solid form as silica or silicates is a direct result of the one-sided affinity relations of the silicon atom," p. 610.

While cuprous chloride solutions are used in gas analysis for absorbing carbon monoxide, it is interesting to note, p. 629, that anhydrous cuprous chloride will not take up nitric oxide; one must have water in order to form $CuCl \cdot CO \cdot 2H_2O$. On the other hand carbon monoxide serves to stabilize anhydrous cuprous oxide, forming $Cu_2SO_4 \cdot 2CO$. The colors of the metal carbonyls vary surprisingly, and without any obvious reason, with the nature of the metal: $Fe(CO)_4$, green; $Fe_2(CO)_6$, gold; $Co(CO)_4$, orange; $Mo(CO)_6$, colorless; $Ru(CO)_2$, brown; and $Ru(CO)x$, pink to orange.

Of course there are short-comings, some natural and some rather unexpected. Weiser's work on phosphorus has been overlooked, p. 76, and the new method of making fluorine, p. 106. Under aluminum, p. 131, the author apparently believes that one could get aluminum if desired by electrolyzing cryolite, whereas cryolite is the sodium salt of alumino-ferric acid and sodium comes off at the cathode when this salt is electrolyzed. From the text one would imagine that people add aluminum chloride to the bath to prevent the action of fluorine on the anode and then add aluminum oxide to prevent the evolution of chlorine. On p. 142 is the statement that zinc cannot be obtained economically by electrolytic methods, which will be interesting news to the Anaconda people. It is quite erroneous to state, p. 146, that from an equimolecular copper-zinc solution, one gets a brass containing eighty per-cent copper unless one mentions the electrolyte. From such a sulphate solution one would get only copper. From the text, p. 170, one would gather that hydrated salts are always stable at their melting-points, whereas that is more often not the case. One should not lump sodium aluminate and sodium chromite together, saying that the solutions consist essentially of free alkali and colloidal oxide, p. 348. That is true for chromic oxide but not for alumina. On p. 581 is the statement that one gets nitrogen peroxide very conveniently by dropping formaldehyde into concentrated nitric acid. The reviewer does not question the accuracy of the observation; but this way of presenting the facts ignores the fact that nitrogen peroxide is probably not a direct reduction product of nitric acid. Under oxidation of ammonia, p. 534, there is no mention of the work of Parsons.

The reviewer objects also to a paragraph on p. 694. "As is well-known, alloys look outwardly very much like pure metals. It is an interesting fact that crystals often do not separate in a polyhedric form from the melt, but come out in rounded forms because they have very high surface tensions, at least at high temperatures, and these surface tensions overpower the crystallizing forces. The surface tension decreases with falling temperature and therefore a compound comes out more spherical at higher temperatures and more crystalline at lower temperatures. From a copper-bismuth melt, copper separates in rounded forms above 800°; but in polyhedric forms at lower temperatures."

The surface tension of liquids decreases with rising temperature. We do not know anything about the surface tension of solids; but there is no reason to suppose that it increases with rising temperature. It is quite possible to define the melting-point as the temperature at which surface tension becomes too strong for the crystallizing forces without postulating that the surface tension increases with rising temperature. The proper assumption is that what we are calling the crystallizing force becomes weaker with rising temperature.

Wilder D. Bancroft

Theoretical Chemistry. *By Walther Nernst. Translated by L. W. Codd. Eighth-Tenth German edition. 22×15 cm; pp. xx+922. New York and London: Macmillan and Co., 1923. Price: $7.00.* "The present translation is based upon the 8th-10th German edition. Eight years have elapsed between this and the previous edition. This fact, together with the important advances of the past few years in various branches of physics and chemistry, necessitated an unusually thorough revision, and additions have been made to several chapters to bring the book up to date. Among the more important additions are the sections dealing with the structure of atoms, the applications of X-ray spectroscopy, and the determination of molecular dimensions. The chapters on radioactivity and the theory of the solid state have been largely rewritten, and many minor additions are also to be found."

The translator has republished the original preface but has omitted the later ones in which it was stated that the volume was dealing more and more with Nernst's own work. Since Nernst's German style was always uncommonly bad, it is a great help to the student to be able to get the subject matter in English.

Nernst apparently does not share the view that reactions produce absorption bands, p. 400. "Baly has put forward the idea that tautomeric equilibrium gives rise to specific absorption bands. He supports this by the observation (*inter alia*) that neither the enol nor the keto form of acetoacetic ester shows by itself an absorption band, but that under the conditions when a tautomeric equilibrium, *i.e.* a quick mutual transformation, exists, an absorption band appears. But the fact that no similar phenomena have yet been found to attend chemical equilibria makes it more probable that the tautomeric change is accompanied, perhaps to a very small extent, by the formation of new molecular species, which give rise to the absorption."

Wilder D. Bancroft

LEUCOPLASTS: LIVING, REPRODUCING, PERFECT CHEMICAL CATALYSTS*

BY EDGAR J. WITZEMANN

It is the purpose of this paper to visualize in chemical terms the familiar operations of leucoplasts as perfect living chemical catalysts. It is hoped, by restating the familiar in these physical chemical terms, that the viewpoint developed may constitute a preparation for a similar visualization of other chemical catalyses in living cells. This paper is also intended to be a contribution to the study of the transition from crystalloid to colloid properties previously discussed in broader terms[1].

(1). *Introduction.* Among the enzymes best known chemically are those that are normally secreted into the gastro-intestinal tract. The conditions by which the activities of these enzymes are modified are pretty well known, so far as the hydrolytic phase of their activities is concerned. On the contrary little is known about the reverse effect—namely condensation—as exercised by these enzymes in conditions that may be considered normal for life[2]. More is known about the synthesis of esters by lipase than any of the condensation reactions here involved[3]. This may be due to the fact that the simpler chemical constitution of fatty acids renders them more immune to slightly unfavorable conditions than the sugars and amino acids, for instance. But whatever the reason, it is well known that these enzymes do not reverse the reaction to the point of equilibrium. They are therefore lacking in this important characteristic of a perfect chemical catalyst. One of the simplest possible explanations of this fact is the idea that chemical investigation has not yet surrounded these hydrolytic enzymes with the proper conditions, in order to enable them to synthesize their substrats as efficiently as they hydrolyse them. This suggestion is also supported by the fact that synthetic reactions are carried out almost entirely within the cells by enzymes *in situ.* The question at once arises as to whether we can view the chemical operations of any enzyme *in situ* with sufficient accuracy to determine whether it is a more perfect chemical catalyst under these conditions than in *in vitro* conditions. This paper constitutes a review of the best known chemical and biological facts concerning the synthesis and hydrolysis of starch in the living plant cell. The results clearly suggest that the enzyme functioning *in situ*, in this case, is more perfect in the accepted physical chemical sense than the common enzyme preparations with which we normally work.

(2). *How is starch formed?*[4] The commonest, readily hydrolysed, polysaccharides are the starch of plants and the glycogen most commonly found in animals. They differ most strikingly, however, in that the latter is generally

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*Contribution from Otho S. A. Sprague Memorial Institute, Rush Medical College, Chicago, Ill.

an invisible jelly while the former is made up of visible sphero-crystals. The formation of the former has been much studied and is easily observed in comparison with the formation of the more gelatinous glycogen in animal tissues. In plants starch appears in two visible relations. It appears temporarily as very small grains in protoplasm and in chloroplasts whenever sugar accumulates locally and it appears as larger more permanent starch grains in connection with those other protoplasmic corpuscles known as leucoplasts. The young starch grain generally appears in the center of the leucoplast as a spherocrystal. Later the leucoplast often tends to become thicker on one side and the crystals assume various shapes depending on the circumstances. The situation may be graphically stated thus: The leucoplast is lying in a dilute solution of sugar while in its interior it is laying down (secreting)[5] a stable condensation product—starch—and is producing thereby a relatively enormous concentration of inert sugar locally. In chemical terms the leucoplast is a catalyst for condensation which has the power of selectively removing sugar from dilute solutions. There is nothing unusual in finding a system acting as a catalyst one of whose properties is the capacity to raise the concentration of a component of the substrate upon its surface or within its boundaries. The action of the leucoplast in this respect therefore coincides with what the colloid chemist calls adsorption. This adsorption like that of the colloid chemist may be positive or negative depending on the concentration of the sugar solution with which the leucoplast is in equilibrium. When the sugar concentration outside the leucoplast falls through a slight range to a point below a certain critical level the adsorption becomes negative in sign and the starch grains begin to undergo erosion. The main difference between the classical adsorption of chemistry and that of the leucoplast is that the condensation brought about by the latter is visible as starch, while in adsorption phenomena in general the fact that condensation or concentration occurs must be deduced mathematically[6].

The leucoplast thus constitutes an ideal chemical catalyst in that it catalyses the reaction in both directions depending upon changes in the environmental conditions one of which is a slight change in the concentration of the sugar solution in which it lies. In this sense it may also be considered to be an ideal enzyme for sugar condensation such as has apparently never been isolated or tested under suitable conditions. Moreover since the leucoplast is apparently a somewhat differentiated portion of the general protoplasm[7] we can identify this enzymatic or catalytic process as a chemical function of protoplasm. This identification is also supported by the fact that small granules of starch are said to be formed throughout the protoplasm of the cell upon slight provocation. These granules are more readily dissolved apparently than those formed in the leucoplasts, so that there appears to be some differentiation in this respect also, although this may be due merely to the well known greater solubility or solution tension of small crystals in the presence of larger ones.

3. *Glycogen formation.* Glycogen differs most strikingly from starch in being less sharply differentiated *in situ* in the cell[8], in being hydrolysed with great rapidity after the death of the organism, and is therefore in all ways more difficult of access. Like starch in plants, glycogen is present to some extent in all parts of the animal organism. The greatest concentration occurs in the liver so that this organ in a sense takes the place of seeds, fleshy tubers, corms, bulbs, etc., of plants as a special storehouse for reserve carbohydrates. The cell "organs" in animals that correspond to the leucoplasts in plants must be very numerous and efficient in the liver. These glycogen-forming elements in the liver have perhaps never been described, but their existence is amply provided for by the complete analogy in all the relations as to constitution, properties, distribution, mobilization, etc., of starch and glycogen.

4. *The role of organization in chemical catalysis.* It may be objected by some that in considering the leucoplast as a catalyst we have moved the problem of condensation in living organisms out of the field of chemistry. This is not true. We have merely acknowledged that a suitable physical state of organization and a suitable chemical environment is more necessary to this catalytic process than is commonly realized. In this respect it then resembles many well-known chemical catalysts which we have become thoroughly accustomed to "petting" in order to sustain their optimal activity. The role of organization in oxidizing catalysts was pointed out by Warburg[9] and by Battelli and Stern[10] and is now generally accepted. Is there any good reason for believing that the unknown oxidizing enzymes and catalysts in general operate on different principles from those concerned with condensation and therefore that one can subject them to any kind of treatment and expect them to retain their activity?

This conception of organization in living organisms involves a suitable physical condition and generally a suitable admixture of other substances. These two conditions must also be met in chemical catalysis. Thus for instance the best catalyst for converting CO into CO_2 at ordinary temperatures is a mixture of four oxides[11], which, for unknown reasons, works better than any of the components taken alone. The fact that a leucoplast is an organized mixture of substances in a suitable condition can therefore not be used as an argument against its being a chemical catalyst.

5. *What makes the condensation reversible?* We have pointed out above how the larger starch grains are found in leucoplasts while those occurring in the general protoplasm are usually smaller. We have noted how rapidly they are formed or disintegrated depending on conditions. We have also pointed out the fact that the variations in concentration of the sugar in the cell sap are sufficient, in terms of the little that we know about adsorption, to account for the change in sign of the adsorption (negative $\rightleftarrows$ positive) with fluctuations in the sugar concentrations. On the other hand it is well known that other components of the medium vary in concentration fully as much as the sugar does, that variations in the concentration of other substances modify the velocity of catalytic processes and that sugar is certainly not the only sub-

stance that can be differentially adsorbed by a leucoplast or by protoplasm in general. Thus it is well known that H^+ ions favor hydrolysis and OH^- ions are unfavorable to the hydrolysis of starch. If the concentration of these ions or their biological analogs varies in the medium then they will be adsorbed by the leucoplast in variable amounts and give rise to a secondary acceleration or retardation of the corresponding process in question. It is in this way and at this point that the presence or absence of internal secretions, etc., probably acts to inhibit or accelerate the hydrolysis or the formation of glycogen in animals. The variations of the concentration of these compounds in the medium gives rise to secondary variations in particular zones of chemical action depending on the adsorption relations of the phases in question to the chemical substances involved.

These accessory agencies do not complicate the chemical picture of the simple underlying chemical processes. They take up the "slack" or "lost motion" of the finer adjustments of the equilibrium and provide a mechanism for more readily maintaining the equilibrium concentrations whenever they are disturbed. To attempt to discuss them in detail now, even if we were prepared to do so, would merely help us lose sight of the simplicity of the fundamental catalytic process.

6. *The condensation hydrolysis equilibrium involved in the formation and mobilization of starch.* The central point of interest in the chemical mystery of the formation of starch is the actual formation and deposition of the polymer starch. Plant physiologists have demonstrated repeatedly that a leaf that has been completely freed from starch by etiolation synthesizes enough starch from CO_2 or sugar solutions in a few minutes after exposure to sunlight to give a positive iodine test for starch. In the hands of the chemist glucose can be slowly converted into polysaccharides only with the greatest difficulty[12]. There are in this respect two types of substances (1) those like water that polymerize and depolymerize freely and spontaneously, and (2) those like sugars that do not. If a substance naturally belongs to the second class there is very little that the chemist can do at present to move it into the first class, because the general subject of the catalysis of condensation equilibria is still wrapped in darkness. One interesting thing however stands out clearly: in plants, and probably in animals, glucose belongs to the first class. If we attempt to explain this difference in the two environments we presently hit upon the idea that perhaps substances of the second class require "preparation" for condensation such as is supplied by insulin in animals in the metabolism of glucose. The most effective agencies for catalysing chemical condensations *in vitro* are weak alkalies like ammonia, pyridine and alkali compounds in general. These are generally thought to give rise to a certain amount of highly reactive isomers, such as the enol forms of certain ketone derivatives, which then condense spontaneously.

Without attempting to review the present unsatisfactory state of this problem in organic chemistry it is even now clear in about what direction the solution of this mystery of spontaneous condensation is to be sought, although the answer can not be concretely discussed or demonstrated *in vitro* as yet.

7. *How are leucoplasts formed?*[13] In considering leucoplasts chemically we ought if possible know how they are made.

Botanists generally believe that most starch is produced by leucoplasts (which they consider to be chloroplasts without chlorophyll), which are multiplied and transmitted from cell to cell by division and are not formed *de novo*[14]. The more recent view is that they arise by a demonstrable differentiation of "mitrochondria" (chondriosomes) which in turn have been observed in all the cells of the plants studied at all stages of development (even in pollen grains)[15].

The chemical differentiation involved is probably not great because it can only be demonstrated by the most recent and painstaking histochemical technique. But if either of these views is correct the formation of leucoplasts is chemically simple.

The existing leucoplasts simply grow by the addition of material until they become large enough to break up or divide due to the fundamental causes that make any particles in an emulsion break up. It is not hard to add material to one phase in a system without appreciably changing the composition of another phase. Or in other words a given phase may grow in size and change in composition without appreciable growth or change in any other phase in contact and in equilibrium with it. Thus if we add oil to an ether solution of oil-in-water suspension we find, when the phases separate so that we can measure their volumes, that the ether layer has been increased. Very little oil dissolved in the water. If water is added instead of oil the results are equally simple but reversed. Moreover our illustration shows us that the phase that is increased is determined by the solubility relations of the component offered to the system. Leucoplasts can and no doubt do have a selective adsorption for some of the compounds of which they are built up (as well as for sugar) that will be great enough to cause them to grow in a true physiological sense[16]. There is abundant chemical experience with systems that behave in the same physical ways that living systems such as leucoplasts do. Moreover the outward similarity persists down to the observable limits of small objects. But no such systems however similar they are outwardly carry the physiological traits of life. Our interest in these analogies is great however because they give us a clear picture of how our living enzyme or leucoplast can function, grow and multiply without requiring us to believe that it does so by virtue of a chemical behavior entirely unknown to us.

The botanist's conviction that leucoplasts increase by division and that they are passed on from cell to cell practically in a preformed condition simplifies the whole problem as to their origin and existence in cells. The problem of increasing their number and activity then becomes one of suitable nutrition of those already present. Considerable progress has been and is being made in the study of enzymes by studying the nutritional factors that are associated with their minimal or maximal activity.

If on the other hand we accept the dissenting view, for which there is also considerable support[17] that although leucoplasts divide, they may also arise *de novo* in the cytoplasm, the chemical conditions of their formation are materially and favorably changed. Under the former view promotion of development of leucoplasts by nutrition is hopeless if there are no leucoplasts present in the cell which can undergo division. Under the latter view it should be possible to promote their formation *de novo* by suitable nutritional adjustments in cases in which they were entirely absent from some of the cells.

8. *Application to diabetes.* Aside from its interest in giving another clear view in the chemical study of enzymes the above discussion of the chemical nature of leucoplasts is of interest in the study of diabetes. The analogies of the formation of glycogen and of starch are, as was stated above, close. It has recently been found that the formation of glycogen can be restored in diabetes by the administration of insulin and it is therefore possible that insulin is an indispensable component of the "glycogen leucoplast" system. In fact the recent isolation of insulin-like materials from yeast[18], from various other plants, from animals and from animal organs suggests that it may be a fundamental component of protoplasm and perhaps a component of true leucoplasts. The available facts concerning insulin indicate that it resembles enzymes in a general way. It is known that enzyme formation and enzyme activity are modified by nutrition. These and other facts, that we need not stop to enumerate, raise the important question as to whether the growth and development of the various catalysts or enzymes involved in diabetes can be improved or restored, by suitable nutritional considerations. There are enough indications that this question is capable of an affirmative answer to justify a long search, by those who have the experimental material in hand, for the definitive factors involved.

9. *Energy relations.* After having made a qualitative survey of the problem of starch and glycogen formation it is well to check up on the energy relations. As soon as we turn to consider the problem in such terms it becomes almost glaringly obvious that the processes of the leucoplast as pictured in this paper show a beautiful conformity to the Law of Supply and Demand otherwise known in chemistry as LeChatelier's Principle. This interesting generalization is stated by Lewis[19] as follows: "When a factor determining the equilibrium of the system is altered the system tends to change in such a way as to oppose and partially annul the alteration in the factor". This law is a qualitative statement of the Second Law of Thermodynamics and as such is probably the most widely applicable generalization known concerning natural phenomena[20].

The most obvious factor involved in the phenomenon of condensation and hydrolysis here under discussion is the close relationship between the ebb and flow of sugar into the leucoplast and the supply and demand of sugar from other parts of the plant. There is here a spontaneous natural equilibrium between kinetic energy just stored in the form of potential energy as newly formed sugar, a less labile type of potential energy as starch and a more labile form of potential energy as mobilized starch. Probably the newly formed sugar and mobilized starch are identical isomers of glucose. In other words we have an equilibrium involving two forms of potential energy obviously controlled by the Second Law of Thermodynamics, which is strikingly visualized by the supply and demand concept. This principle of the chemical philosophy of plants may be graphically represented thus:

$$\left.\begin{array}{l}\text{Chemically labile,}\\ \text{physically stable but diffusible,}\\ \text{dialysable glucose.}\end{array}\right\} \rightleftarrows \left\{\begin{array}{l}\text{Physically labile,}\\ \text{chemically stable,}\\ \text{non-diffusible, non-dialysable}\\ \text{starch.}\end{array}\right.$$

This equilibrium also visualizes an interesting differentiation of energy which was more fully discussed in general terms in a previous paper[21]. If we consider glucose and starch as two closely related forms of potential energy we have in the low glucose concentration of the cell plasma an equally low intensity of energy concentration, while with starch we have a highly concentrated form of glucose with a corresponding high intensity of potential energy. Since hydrolysis is said to be an exothermic reaction energy used up in the "work" of condensation must be derived from some other source. In the case of the leucoplast this may arise from the oxidation of part of the sugar.

The tremendous simplicity and efficiency of the energy relations involved here and the perfect "team work" with which the leucoplast "plays up" to the chloroplast become more overpowering the longer one considers them. It sometimes seems that if anything in the world is a more perfect physical chemical mechanism than one of these it is undoubtedly the other.

Summary

By considering the leucoplast as the enzyme which catalyses the starch-sugar equilibrium we clarify the whole problem of enzymatic condensation for ourselves and escape a number of difficulties.

(1) Our enzyme is a perfect catalyst in a physical chemical sense.

(2) It functions as a segregated corpuscle which is visible in the living cell and can not therefore be an artifact arising from post-mortem changes.

(3) It represents a differentiated function that is not so efficiently performed by protoplasm as a whole.

(4) It multiplies within the cell by division (generally).

(5) Its efficiency is no doubt due to its chemical constitution and its physical state of organization. Press juice containing leucoplast juice and other material more uniformly mixed could not *a priori* be expected to function well in the formation of starch though it might hydrolyse polysaccharides rather well.

(6) In this respect the leucoplast resembles the better known chemical catalysts (like platinum) which are highly active under suitable conditions but not so active or even entirely inactive under other conditions.

(7) It is also interesting to note that the problem of condensation when viewed in its structural relations in this way parallels the observations of Warburg on the role of structural organization in vital oxidation.

In the later sections of the paper the possible existence of glycogen forming leucoplasts is briefly considered on the basis of analogy. The existing viewpoints on the origin of leucoplasts are further extended in order to discuss their formation in the cell. From any of the existing viewpoints as to their formation the problem of the primary formation and multiplication of such organized catalysts is for the present still a problem in nutrition.

The qualitative relations developed conform in interesting ways with the qualitative statement of the Second Law of Thermodynamics known as Le Chatelier's Principle. Furthermore the glucose $\rightleftarrows$ starch equilibrium involves an interesting differentiation of potential energy.

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[1] E. J. Witzemann: J. Phys. Chem. **26**, 201 (1912).

[2] We know that condensation is quantitatively one of the most abundant as well as one of the most delicately adjusted types of reactions that take place in the living organism. All higher life is organized on that basis. Condensation is the reaction that enables life to persist during periods of unfavorable fluctuations in the food supply. The facts are glaringly obvious from any point of view and yet we can not interpret them chemically because we know little or nothing about condensation, even in chemistry.

[3] Cf. W. M. Bayliss: "The Nature of Enzyme Action". 3rd Ed. Chapter on reversibility of enzymes for other examples and fuller discussion.

[4] The botanical facts here given will be found in J. Reynolds Green's "Vegetable Physiology," p. 224, 2nd Ed. (1907) or in F. Czapek's "Biochemie der Pflanzen," I, 397-417 (1913). A more extended review of the subject of starch is given in E. T. Reichert's Monograph: "The Differentiation and Specificity of Starches in Relation to Genera, Species, etc. Carnegie Institution of Washington, Publication No. **173**, pp. 17-163 (1913).

[5] J. Reynolds Green: "Vegetable Physiology," p. 228, 2nd Ed. (1907).

[6] W. D. Bancroft: "Applied Colloid Chemistry," p. 24, for example.

[7] Cf. especially A. Guilliermond: Arch. Anat. Micro. **14**, 309-428 (1913) on the formation of leucoplasts by differentiation of mitochondria (Chondriosomes).

[8] J. Reynolds Green: "Vegetable Physiology," p. 232. Glycogen in fungi sometimes separates as granules, "which to a certain extent resemble grains of starch and which have been stated to originate in certain corpuscular bodies resembling leucoplasts. In most cases the deposition appears to be effected by the protoplasm".

[9] O. Warburg: Erg. der Physiol. **14**, (1914).

[10] Biochem. Z. **67**, 443 (1914).

[11] A. B. Lamb, W. C. Bray, and J. C. W. Frazer: J. Ind. Chem. Eng. **12**, 213 (1920).

[12] J. U. Nef: Ann. **403**, 223 (1914).

[13] See Lester W. Sharp: "An Introduction to Cytology," pp. 104, 106, 109, 113, 121, 122, (1921) for a summary of the present status of the various views on the nature and origin of leucoplasts.

[14] "There are some other small bodies which are free from coloring matter, and which form starch from sugar. We call all these protoplasmatic organs which are in the service of carbohydrate metabolism, *Plastids*. As far as we know, they are never formed from other plasmatic parts. They always take their origin from mother plastids by cleavage". F. Czapek: "Chemical Phenomena in Life," p. 59.

[15] Cf. Guilliermond: *Loc. cit.*

[16] The capacity of growth of leucoplasts presupposes a selective adsorption by leucoplasts of the components of which they are synthesized . This however represents the transition from crystalloid to colloid properties within homologous series previously discussed. Without attempting to discuss the case in detail we have here an apparently spontaneous transition from the crystalloid state to the colloid state of the components of leucoplasts for the development of a catalyst (the leucoplast), adapted to enormously facilitate the transition of crystalloid sugar into colloidal starch and *vice-versa*. So far as present knowledge goes the formation of the leucoplast is an autocatalysis.

[17] Cf. Sharp: Loc. cit. p. 118.

[18] L. B. Winter, and W. Smith. (Proc. Physiol. Soc.) *J. Physiol.* **57**, XL (1923).

[19] Wm. C. McC. Lewis: "A System of Physical Chemistry," Vol. II, p. 109, 3rd Ed. (1920).

[20] Cf. W. D. Bancroft: J. Am. Chem. Soc. **33**, 91, (1911) and W. C. McC. Lewis: Loc. cit.

[21] E. J. Witzemann: J. Phys. Chem. **26**, 201 (1922).

STUDIES ON ADSORPTION. V

Coagulation of Negatively and Positively Charged Ferric Hydroxide Sols and of Negatively Charged Antimony Sulphide Sol by Electrolytes

BY K. C. SEN, P. B. GANGULY AND N. R. DHAR

In previous parts of this series of papers[1] several cases of charge reversal by electrolytes have been investigated.

It has been shown in those communications that arsenious acid peptises freshly precipitated ferric hydroxide into a negatively charged sol, and it appears probable that the arsenite ion is the active agent in the peptisation. Biltz[2] studied the adsorption of arsenious acid by ferric hydroxide on precipitating a sol by means of ammonium salts in presence of arsenious acid and showed that the results agree with an adsorption isotherm. Later on, Lockemann and Paucke[3] studied the adsorption of arsenious acid by hydrated ferric oxide. Their method of experiment was to mix a solution of ferric chloride with the acid, and then to precipitate the ferric hydroxide by means of ammonia. They showed that ferric hydroxide adsorbs a great amount of arsenic. It will be observed that in both the methods, there are considerable quantities of ammonium salts present. We decided to repeat these experiments using caustic soda as the precipitating agent to see whether the amount of adsorption changes with the change of electrolyte. When, however, the theoretical quantity of alkali was added to a mixture of ferric chloride and arsenious acid, there was no precipitation of the hydroxide, nor did a slight increase in the amount of alkali cause precipitation. On repeating the experiment with ammonia as the precipitating agent, an immediate precipitation of ferric hydroxide was obtained.

In view of this surprising result, the subject has been thoroughly investigated. It has found that by using caustic soda as the precipitant, when the amount of As_2O_3 in solution exceeds about 0.40 grm per 1 gr of Fe_2O_3, a colloidal solution of ferric hydroxide is obtained. If the proportion is less, partial colloid formation takes place. Concentrated sols containing 10-12 grms Fe_2O_3 per litre have been prepared simply by taking a concentrated solution of ferric chloride mixed with the proportionate quantity of As_2O_3 and adding a slight excess of caustic alkali. The mixture is then dialysed.

The sol is negatively charged and sodium chloride or sodium hydroxide, unless in very high concentrations, has a very small coagulating power on this sol. Ammonium salts cause immediate precipitation and this explains the fact

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[1] Sen and Dhar: Kolloid-Zeit. (1923), Dhar and Sen: J. Phys. Chem. (1923).

[2] Ber. 37, 3138 (1904).

[3] Kolloid-Z. 8, 273 (1911).

that the experiments of Biltz and of Lockemann and Paucke could only be successful because they used ammonium salts and ammonia as the precipitating agents. The sol is extremely sensitive to bivalent and trivalent electrolytes, and is very suitable for coagulation experiments. That it is really a case of charge-reversal has been shown by taking positively charged sol prepared by the ordinary method of boiling a ferric chloride solution, adding the requisite quantity of arsenious acid, and then mixing it with caustic soda solution, slightly in excess of that required theoretically. Arsenious acid acts as a protecting agent, and no coagulation occurs. It has been already shown that negatively charged ferric hydroxide can be obtained by the *action* of alkali on a mixture of a ferric salt and glycerine or sugar[1]. Moreover, it was also been stated that arsenious acid can peptise freshly precipitated ferric hydroxide to a negatively charged sol. Evidently the above method of preparation as described in this paper is really a joint action of the two peptizing agents.

I. Preparation of the negatively charged Ferric Hydroxide Sol.

10 cc of $FeCl_3$ solution containing 0.5 gram Fe_2O_3 (about 1.88N) was mixed with 75 cc $As_2O_3N/16.07$ solution and put in a stoppered bottle; 25 cc of normal caustic soda was slowly added to the bottle, and the bottle was vigorously shaken. The sol was perfectly clear and of a dark reddish-brown colour. On standing for two days, the sol was dialysed through a parchment dialyser with frequent changes of external water. After about six days the sol was practically free from chloride. The external water showed no turbidity when treated with silver nitrate. On taking a portion of the sol and dissolving the iron in nitric acid, and adding silver nitrate, very slight opalescence was observed after sometime. This very small quantity of chloride could not be got rid of by further dialysis. Large amounts of arsenious acid, however, remained with the colloid, which could not be removed. The charge on the sol was found to be negative. Measured quantities of this sol were diluted and used for coagulation experiments. The sol was not alkaline to litmus. Stable, negatively charged ferric hydroxide sol can be readily obtained by shaking aqueous solutions of sodium arsenite or of sodium tartrate, or of sodium citrate with freshly precipitated and well washed ferric hydroxide. The effect of solutions of other electrolytes on freshly precipitated ferric hydroxide is being investigated. Several investigators have studied the conductivity of positively charged colloidal ferric hydroxide. Duclaux[2] proved that this sol has a fairly high conductivity. By filtering the colloid through collodion membranes, it was found that the conductivity of the filtrate was not appreciable.[3] Pauli and Matula[4] have applied the micelle theory to this colloid. We determined the conductivity of the negatively charged sol and the following table gives the conductivity data of the negatively charged ferric hydroxide

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[1] Sen and Dhar: loc. cit.

[2] Compt. rend. 140, 1868, 1544 (1905); Kolloid-Z. 3, 126 (1908).

[3] See also Zsigmondy: "Chemistry of Colloids", p. 166 (1917).

[4] Kolloid-Z. 21, 49 (1917).

sol. The original sol was gradually diluted, and hence the concentration of arsenious acid also changed in the same proportion.

Temp. 30° C Conductivity of water used $=6\times10^{-6}$ approx.

Conductivity of N/16.07 arsenious acid $=22\times10^{-6}$, the value is slightly higher than that of Wood[1].

Conc. of Colloid gr Fe_2O_3 per liter		Conductivity
(1)	4.545	244.2×10^{-6}
(2)	2.2725	139.5×10^{-6}
(3)	1.1362	73×10^{-6}
(4)	0.5681	48.8×10^{-6}
(5)	0.2840	30.5×10^{-6}

In view of the fact that no coagulation experiment has yet been made on an ordinary sol, the charge of which has been reversed it was thought advisable to study the effect of different electrolytes on this sol. The results would be interesting because a comparison could be made between the coagulation powers of different electrolytes on the positively charged and the negatively charged sols. The Schulze-Hardy rule can also be verified. The coagulative powers of electrolytes when the concentration of the sol is varied, have also been studied.

In a foregoing paper[2] the coagulation of negatively charged manganese dioxide sol has been investigated from the above points of view.

About eighteen electrolytes have been used in these experiments. The method of determining the minimal concentration of electrolytes necessary for complete coagulation was the titration method of Picton and Linder. 5 cc of the sol was taken from a burette into clean test tubes, and drop by drop the electrolyte was added from a 1 cc pipette calibrated in hundredths of a cc, the test tube being shaken after each addition. It has been observed that whether the electrolyte is added slowly or the whole of it at once, the minimal concentration of electrolyte necessary for coagulation does not change appreciably in the majority of cases; but in some cases there is a slight difference. In these latter cases a mean of several determinations has been taken. The coagulating point is very sharp and hence the titration method of determining coagulation power of electrolytes gives fairly accurate and comparative results. The strength of the electrolytes has been varied so that the resulting volume may not be unnecessarily large thus diluting the colloid to any considerable extent. The coagulative powers have been expressed as the inverse of the number of gram molecules of electrolytes in the total reaction mixture.

The following results were obtained.

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[1] J. Chem. Soc. **93**, 411 (1908).

[2] Ganguly and Dhar: J. Phys. Chem. **26**, 700 (1922).

TABLE I

Strength of the Sol = 0.22725 gr Fe_2O_3 per litre (A/2)
Temp. = 30°C.

Salt	Conc.	Vol. added in cc.	Coagulative Power
KI	N/10	0.28	188.6
NH_4Cl	N/10	0.13	395.2
KBr	N/10	0.22	237.5
KCl	N/10	0.485	113.1
KCNS	N/10	0.24	219.2
NaCl	N/5	0.41	65.9
K_2SO_4	N/10	0.249	105.49
NaOH	N	0.39	13.8
HCl	N/100	0.06	8474
$AgNO_3$	N/111	0.05	11211
$BaCl_2$	N/101	0.02	1269
$SrCl_2$	N/10	0.035	725
$HgCl_2$	N/100	0.06	4219.4
$CeCl_3$	N/100	0.035	4796
$MnSO_4$	N/100	0.02	12562.5
$ZnSO_4$	N/10	0.01	2512.5
$UO_2(NO_3)_2$	N/10	0.01	2512.5
$Al_2(SO_4)_3$	N/100	0.015	11148.

TABLE II

Strength of the Sol = 0.4545 gr Fe_2O_3 per litre (A)
Temp. = 30°C.

Salt	Conc.	Vol. added in cc.	Coagulative Power
KI	N/10	0.54	100.6
NH_4Cl	N/10	0.27	195.5
KBr	N/10	0.39	138.2
KCl	N/10	0.85	68.82
KCNS	N/10	0.48	114.1
NaCl	N/5	0.82	34.9
K_2SO_4	N/10	0.52	53.09
NaOH	N	0.74	7.7
HCl	N/100	0.125	4098
$AgNO_3$	N/111	0.13	4380
$BaCl_2$	N/10	0.02	1269
$SrCl_2$	N/10	0.055	460
$HgCl_2$	N/100	0.10	2550
$CeCl_3$	N/100	0.08	2115.3
$MnSO_4$	N/100	0.04	6305.1
$ZnSO_4$	N/10	0.015	1672
$UO_2(NO_3)$	N/10	0.03	838.9
$Al_2(SO_4)_3$	N/100	0.065	2598

TABLE III

Strength of the Sol = 0.909 gr Fe_2O_3 per litre (2A)
Temp. = 30°C.

Salt	Conc.	Vol. added in cc.	Coagulative Power
KI	N/10	0.45	121.1
NH_4Cl	N/10	0.28	188.5
KBr	N/10	0.41	131.9
KCl	N/10	0.91	64.9
KCNS	N/10	0.53	104.2
NaCl	N/5	0.80	36.2
K_2SO_4	N/10	0.60	53.55
NaOH	N	0.51	10.8
HCl	N/100	0.19	2732
$AgNO_3$	N/111	0.085	6660
$BaCl_2$	N/10	0.02	1269
$SrCl_2$	N/10	0.055	460
$CeCl_3$	N/100	0.10	1700
$HgCl_2$	N/100	0.195	1332
$MnSO_4$	N/100	0.045	5611.5
$ZnSO_4$	N/10	0.015	1672
$UO_2(NO_3)_2$	N/10	0.04	630.5
$Al_2(SO_4)_3$	N/100	0.08	2117.6

TABLE IV

Showing the Variation of Coagulative Powers with the Concentration of the Sol.

Salt	Conc. of Sol. = A/2 (0.22725 gr Fe_2O_3) per litre	Conc. of Sol. = A Coagulative Power	Conc. of Sol. = A2
KI	188.6	100.6	121.1
NH_4Cl	395.2	195.5	188.5
KBr	237.5	138.2	131.9
KCl	113.1	68.82	64.9
KCNS	219.2	114.1	104.2
NaCl	659	34.9	36.2
K_2SO_4	105.49	53.09	53.55
NaOH	13.8	7.7	10.8
HCl	8474	4098	2732
$AgNO_3$	11211	4380	6660
$BaCl_2$	1269	1269	1269
$SrCl_2$	725	460	460
$HgCl_2$	4219.4	2550	1332
$CeCl_3$	4796	2115.3	1700
$MnSO_4$	12562.5	6305.1	5611.5
$ZnSO_4$	2512.5	1672	1672
$UO_2(NO_3)_2$	2512.5	838.9	630.5
$Al_2(SO_4)_3$	11148	2598	2117.6

II. Preparation of positively charged Ferric Hydroxide Sol.

The sol was prepared after the manner of Krecke[1] by the gradual addition of a concentrated solution of ferric chloride to a large volume of boiling water which was kept well stirred. The sol did not give anycolouration with potassium ferrocyanide. The sol, however, contains hydrochloric acid and to remove it, it was dialysed. After six days the dialysed sol was found to be free from electrolytes. The dialysed sol was found to have gained in intensity of colour and it could be concentrated to any desired strength by boiling.

2 N solutions of potassium nitrate and barium chloride; N/200 solutions of zinc sulphate, cadmium sulphate, potash alum, magnesium sulphate, potassium oxalate, N/2000 solution of sodium citrate, N/4000 solution of potassium ferricyanide, N/3.4 solution of potassium hydroxide and 1.2N solution of hydrochloric acid, were prepared. The quantities of these electrolytes necessary to coagulate 5 cc of the ferric hydroxide sol were determined by a series of trial experiments. 5 cc of the ferric hydroxide sol were placed in each of several test tubes. Measured quantities of the electrolytes were run into a series of labelled tubes, the volume in each of which was made up to 6 cc with addition of water where necessary. The electrolyte solutions were then rapidly added to the sol and the two thoroughly mixed by transferring from one tube to another several times. The strength of the ferric hydroxide sol was determined by coagulating the sol by means of ammonium chloride and then weighing the dried coagulum as Fe_2O_3. The experimental results are given in the following tables.

TABLE V

Dialysed Sol

Strength of Sol = 0.25 grm of Fe_2O_3 per litre (A/2)

Electrolytes	Conc.	Vol. required for coagulation
KNO_3	2N	3.0 cc
$BaCl_2$	2N	3.2 cc
HCl	1.2 N	4.9 cc
KOH	N/3.4	0.8 cc
$ZnSO_4$	N/200	0.65 cc
$CdSO_4$	N/200	0.60 cc
$MgSO_4$	N/200	0.80 cc
K. Alum	N/200	0.75 cc
K_2. Oxalate	N/200	0.6 cc
Na_3. Citrate	N/2000	3.2 cc
$K_3Fe(CN)_6$	N/4000	3.5 cc

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[1] J. prakt. Chem. 3, 286 (1871).

TABLE VI

Dialysed Sol (A)

Strength of Sol = 0.05 grms of Fe_2O_3 per litre.

Electrolyte	Conc.	Vol. required for coagulation
KNO_3	2 N	2.75 cc
$BaCl_2$	2 N	3.15 cc
HCl	1.2 N	5 cc
KOH	N/3.4	0.6 cc
$ZnSO_4$	N/200	0.7 cc
$CdSO_4$	N/200	0.7 cc
$MgSO_4$	N/200	0.6 cc
K. Alum	N/200	0.75 cc
K. Oxalate.	N/200	0.58 cc
Na_3. Citrate	N/2000	3.75 cc
$K_3Fe(CN)_6$	N/4000	4.2

TABLE VII

Dialysed Sol

Strength of Sol = 1 gm of Fe_2O_3 per litre (2A)

Electrolyte	Conc.	Vol. required for coagulation
KNO_3	2 N	2.5 cc
$BaCl_2$	2 N	2.75 cc
HCl	1.2 N	4.7 cc
KOH	N/3.4	0.5 cc
$ZnSO_4$	N/200	0.75 cc
$CdSO_4$	N/200	0.75 cc
$MgSO_4$	N/200	0.65 cc
K. Alum	N/200	0.8 cc
K_2. Oxalate	N/200	0.75 cc
Na_3. Citrate	N/2000	6 cc
$K_3Fe(CN)_6$	N/4000	6.3 cc

TABLE VIII

Electrolyte	Conc.	Volume required for coagulation			
		Sol A/2	Sol A	Sol 2A	Sol 4A
Potassium Oxalate	N/2000	6.0 cc	5.9 cc	7.8 cc	12 cc

TABLE IX

Electrolyte	*Dialysed Sol* cc. of electrolytes required for coagulation				*Undialysed Sol* cc. of electrolytes required for coagulation		
		Sol A/2	Sol A	Sol 2A	Sol A/2	Sol A	Sol 2A
KNO_3	2 N	3.0cc	2.5 cc	2.2 cc	6.1.cc	5.1 cc	—
$BaCl_2$	2 N	3.2cc	2.75cc	2.5 cc	7.2 cc	5.3 cc	—
$MgSO_4$	N/200	0.8cc	0.6cc	0.65cc	1.6 cc	2.8 cc	—
$CdSO_4$	N/200	0.6cc	0.7cc	0.75cc	1.8 cc	2.4 cc	—

Dialysed Sol

Na_3. Citrate	N/2000	3.2 cc	3.75cc	6.0cc
$K_3Fe(CN)_6$	N/4000	3.5 cc	4.2 cc	6.3cc

III. Negatively charged Antimony Sulphide Sol:

Colloidal antimony sulphide was prepared by Picton[1] about thirty years back. He had also examined its properties, but his observations were purely of a qualitative nature. In the following experiments the coagulating powers of various electrolytes on antimony sulphide sols of three different concentrations have been studied quantitatively.

Preparation of the sol:—

The sol was prepared by a slight modification of the original method of Schulze. A dilute solution of potassium antimony tartrate was slowly dropped from a burette into a saturated solution of sulphuretted hydrogen in water through which a current of sulphureted hydrogen was also being passed. An orange-red sol was obtained which was freed from sulphuretted hydrogen by a current of hydrogen. It was noticed that a very brisk current of hydrogen sulphide at the beginning tended to precipitate some of the antimony sulphide, but after the experiment had gone on for some time, the current of hydrogen sulphide could be made more rapid without any such precipitation. The sol, however, contained tartaric acid and its potassium salt. Attempts were made to remove the acid and its salts by dialysis, but after a fortnight the resulting sol was found more unstable than the original undialysed sol. It was not found possible to prepare stable sols, the antimony content of which corresponded to more than eight grams of antimony potassium tartrate per litre, by this method. Below this concentration, however, quite stable sols are obtained which keep for a considerable period. If kept for some time, mould grows in the solution and carry down certain amounts of the sulphide along with it. Moreover it has been found that time has a very definite aging effect

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[1] J. Chem. Soc. 61, 137 (1892).

on the sol. Hence it is necessary to prepare the sol each time when it is required for use. Fresh solutions so prepared are in all respects quite suited for coagulation experiments

N/5 NaCl and LiCl; N/100 $Co(NO_3)_2$, $Ni(NO_3)_2$, $SrCl_2$, $ZnSO_4$, $MgSO_4$, $Ba(NO_3)_2$ $Pb(NO_3)_2$, $Al(NO_3)_3$; N/10 $Th(NO_3)_4$ and N/25 $UO_2(NO_3)_2$ were prepared. The quantity of each of the above electrolytes that would coagulate 5cc of the sol in four hours, was found out as the result of several trial experiments. 5cc of the freshly prepared sol were placed in the required number of tubes and the necessary amount of electrolyte added by means of a fractional pipette, water being added wherever necessary to bring up to the same total volume. Sols of antimony sulphide of three different concentrations corresponding respectively to 4,2 and 1 grams of antimony potassium tartrate per litre were studied in the above manner.

The experimental results are given in the following table.

TABLE X

		Sol. = 1gr. of antimony pot. tartrate per litre (A)		Sol. = 2gms. of antimony pot. tartrate per litre (2A)		Sol. = 4gms. of antimony pot. tartrate per litre (4A)	
		cc.	Time in hours	cc.	Time in mons.	cc.	Time in hours
NaCl	N/5	1.4	5	.85	4.5	.55	3.5
LiCl	N	.3	4	.25	5	.175	5
$Co(NO_3)_2$	N/100	.45	4	.5	3	.55	5
$Ni(NO_3)_2$	N/100	.5	5	.6	5	.65	5
$SrCl_2$	N/100	.55	3.5	.55	5	.7	4
$ZnSO_4$	N/100	.6	4	.7	5	.75	4
$MgSO_4$	N/100	.4	3	.35	5	.325	4
$Ba(NO_3)_2$	N/100	.5	4	.5	5	.45	3.5
$Pb(NO_3)_2$	N/100	.6	Immediate	.8	Immediate	1.2	Immediate
$Al(NO_3)_3$	N/100	.025	4	.04	4	.05	3.5
$UO_2(NO_3)_2$	N/25	.4	3.5.	.55	4.5	.9	4
$Th(NO_3)_4$	N/10	.225	5	.325	4.5	.575	4

Discussion of Results

An examination of Table I gives the following order for the coagulation powers of different electrolytes on the negative ferric hydroxide sol:—

$MnSO_4 > AgNO_3 > Al_2(SO_4)_3 > HCl > CeCl_3 > HgCl_2 > ZnSO_4 > UO_2(NO_3)_2 > BaCl_2 > SrCl_2 > NH_4Cl > KBr > KCNS > KI > KCl > K_2SO_4 < NaCl > NaOH$

From Table II, the order is:—$MnSO_4 > AgNO_3 > HCl > Al_2(SO_4)_3 > HgCl_2 > CeCl_3 > ZnSO_4 > BaCl_2 > UO_2(NO_3)_2 > SrCl_2 > NH_4Cl > KBr > KCNS > KI > KCl > K_2SO_4 > NaCl > NaOH$; where as Table III gives another order:—

$AgNO_3 > MnSO_4 > HCl > Al_2(SO_4)_3 > CeCl_3 > ZnSO_4 > HgCl_2 > BaCl_2 > UO_2(NO_3)_2 > SrCl_2 > NH_4Cl > KBr > KI > KCNS > KCl > K_2SO_4 > NaCl > NaOH$.

From the experimental results it appears that the Schulze-Hardy law is partially applicable in this case. Thus in the first two tables, divalent manganese comes first and then monovalent silver. In the third table monovalent silver has the greatest coagulative power. Again monovalent hydrogen appears to have great coagulative power, coming between aluminum and cerium in the first table, and before aluminium in both the second and the third tables. Silver and hydrogen both have greater coagulative powers than divalent barium, strontium, zinc, etc. These facts are opposed to the so-called law of Schulze and Hardy. In the case of the positively charged sol, the position of hydrogen is not anomalous as will be shown later on, HCl behaves like other univalent electrolytes; whilst the position of OH′ ion is anomalous in the positively charged sol.

An examination of the three Tables given above also reveals another interesting fact. The concentration of the sol changes markedly the order of coagulative powers of different electrolytes. Thus in Table I(Conc A/2), aluminium sulphate comes before hydrochloric acid, cerium chloride before mercuric chloride, zinc sulphate and uranyl nitrate have equal coagulative powers and come before barium chloride; whereas in Table II (Conc. A) hydrochloric acid comes before aluminium sulphate, mercuric chloride comes before cerium chloride and uranyl nitrate comes between barium chloride and strontium chloride. In Table III (Conc. 2A), however, there is a further change of order. Thus silver nitrate comes off before manganese. Both cerium and zinc come before mercury. Among the monovalent electrolytes potassium iodide comes before potassium thiocyanate. Thus it will be seen that change in the concentration of a colloid affects markedly the precipitating power of electrolytes. Recently, Ganguly and Dhar[1] have also found in the coagulation of manganese dioxide sol change in concentration of the sol has also a great effect on the order of coagulative powers of different electrolytes.

Since the sol is negatively charged it is obvious that the cations are the active agents in coagulation. It is however possible that the anions do take some part, counteracting the effect of the cations to some extent. Thus from the first two tables the order of coagulative powers when the cation is the same is as follows:—$KBr > KCNS > KI > KCl > K_2SO_4$

In the third table there is a slight divergence, KI coming before KCNS. This means that the SO_4 ion has the greatest protective effect, which is as it should be. It appears therefore that in determining the coagulative powers, the effect of the opposite ion must be taken into account.

In some recent papers Burton[2] and his coworkers have shown that for monovalent ions the concentration of ion necessary for coagulation increases with the decreasing concentration of the sol. In the case of divalent ions the values of coagulating power remain approximately the same, in spite of the change in the concentration of the sol, whereas in the case of trivalent ions,

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[1] J. Phys. Chem. 26, 701 (1922).

[2] J. Phys. Chem. 24, 701 (1920); 25, 517 (1921).

there is a direct proportionality between the concentration of the sol and the concentration of the precipitating ion. The curves of the results obtained by us are given herewith (See Figs. 1, 2, 3).

It will be observed that for monovalent ions, there is a steady increase in the coagulative powers of KCl, KBr, KCNS, NH_4Cl, and HCl with decreasing concentration of the sol. With NaOH, NaCl, $AgNO_3$ and KI there is at first a decrease and then an increase. In the case of K_2SO_4 at first it is practically constant and then with further decrease in the concentration of the sol there is an increase in the coagulative power. Ganguly and Dhar (loc cit) have also found, that in the coagulation of MnO_2 sol, the coagulative powers of KI and NaCl at first decrease and then slightly increase. The above results are therefore quite opposed to the rule of Burton and his coworkers.

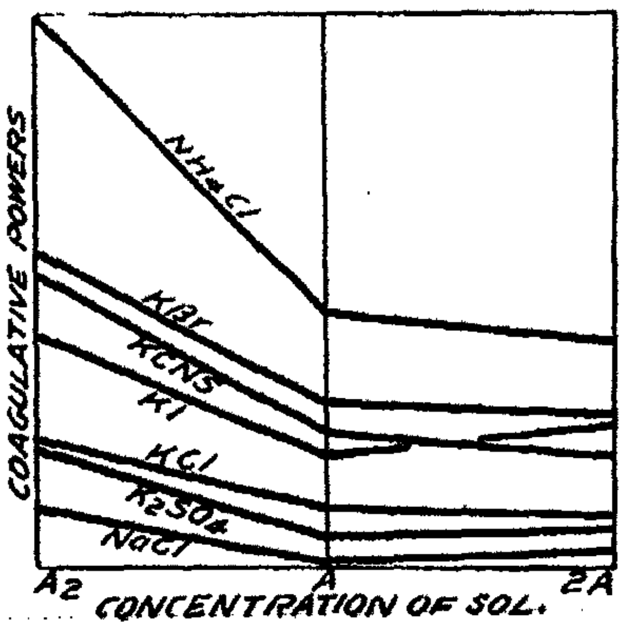

Fig. 1

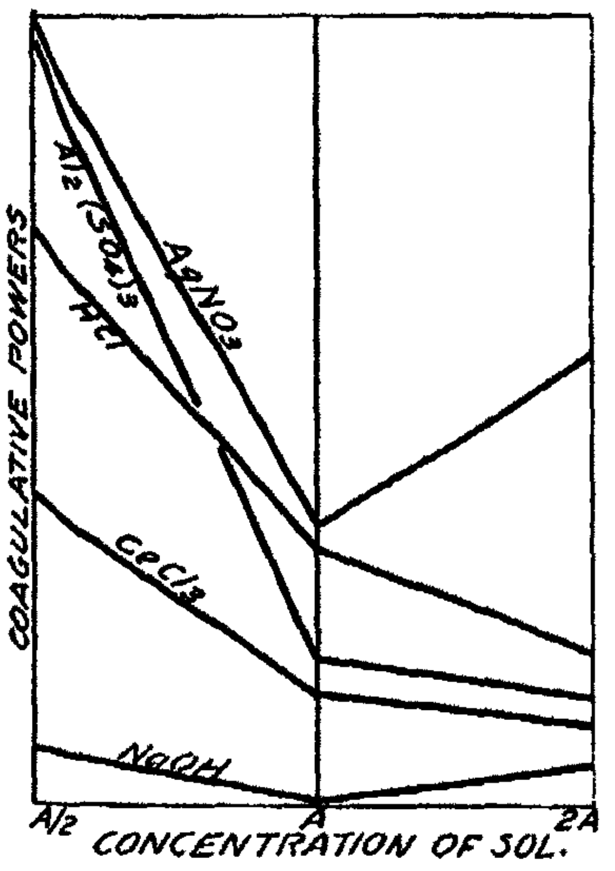

Fig. 2

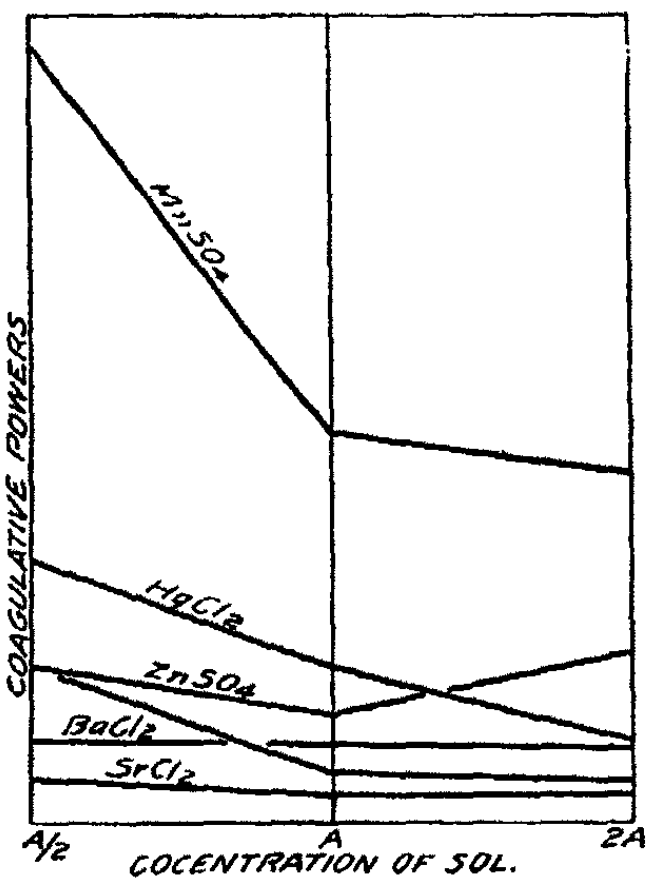

Fig. 3

Sodium chloride and sodium hydroxide have very small coagulative powers, whereas the coagulative power of ammonium chloride is about six times that of sodium chloride.

In the case of bivalent salts, the coagulative powers of barium only remain constant. The coagulative powers of zinc strontium, mercury manganese and uranyl ion rapidly increase with the dilution of the sol. These results are also opposed to the conclusions of Burton and his coworkers.

Two trivalent salts have been examined viz., aluminium sulphate and cerium chloride, and in both the cases, the coagulative powers increase with the decrease in the concentration of the sol.

Applying Whetham's rule[1] to manganese dioxide sol and taking the cases of potassium chloride, cadmium chloride and alum, the ratios between the coagulative powers[2] come to about 1:2:3. In the following table some of the results obtained with negative ferric hydroxide sol are given. The trivalent electrolyte is strontium chloride and the trivalent electrolytes are cerium chloride and aluminium sulphate. X is the coagulative power of the trivalent ion compared to the monovalent ion as 1.

Concentration of Sol.	Monovalent Electrolyte	X	X^2 (Calculated)	X^2 (Coagulative power of trivalent electrolytes) observed	
	KI	4.5	20.25	$CeCl_3$	$Al_2(SO_4)_3$
A	KCl	6.6	43.5	21	25.8
				30.7	37.7
$\frac{A}{2}$	KCNS	4	16.	18.9	22.7
	KCl	6.4	40.9	42.4	—
	KI	3.8	14.44	14.03	17.3
2 A	NH_4Cl	2.3	5.76	8.9	11.06
	KBr	3.4	11.56	12.5	15.5
	KCNS	4.4	19.36	16.3	20.2

It will be observed therefore that in these cases the results agree to a certain extent Whetham's rule. The discrepancies, in other cases, are large and it is well known that the rule is more or less qualitative.

Positively charged ferric hydroxide sol:

The coagulation in this case is brought about by the neutralisation of the charge on the sol by the anions. An examination of the foregoing experimental results shows that the ratio between the coagulative powers of the monovalent nitrate, the divalent sulphate and the trivalent citrate ions are as 1:1000:1500.

There is thus a very marked difference between the coagulative powers of mono, di, and trivalent ions, and in this the Schulze-Hardy law is borne out. But the ratio between the coagulative powers do not conform to the geometric series of Whetham, viz., that the precipitation concentration of mono, di, and trivalent ions are in the ratio of K^3:K^2:K, K being a constant. Thus whilst the divalent sulphate is about 1000 times more active than the monovalent nitrate, the trivalent citrate ion is only 1500 times more reactive than the nitrate. In other words, the trivalent citrate ion is only 1.5 times more active than the divalent sulphate ion. This value is far less than what is required by Whetham's rule.

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[1] Whetham: Phil. Mag. (5) 48, 474 (1899).

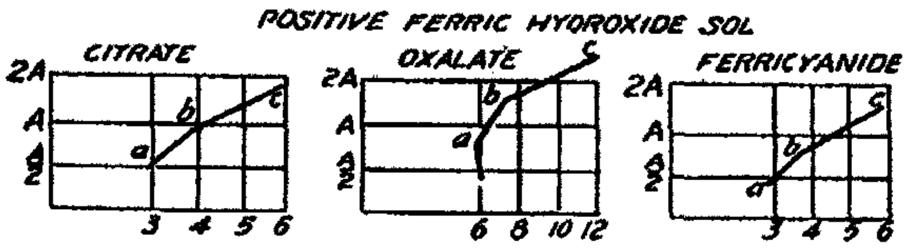
[2] Ganguly and Dhar: loc. cit.

An examination of the volumes of electrolytes required for coagulating sols of ferric hydroxide of different strengths shows that for the monovalent anions nitrate and chloride, the quantity of electrolytes required for coagulation gradually increases as the sol becomes more and more dilute and so far it follows Burton and Bishop's rule (loc cit). The difference, however, between the volumes of the monovalent electrolytes is not very great. Thus as the concentration of the ferric hydroxide sol becomes double, the quantity of potassium nitrate decreases from 3 .cc to 2.75 cc., which further decreases from 2.75 to 2.5 cc when ferric hydroxide sol becomes four times as strong.

With divalent electrolytes as the concentration of the colloid increases, the quantity of electrolyte required for coagulation of the colloid also gradually increases, thus as the concentration of the colloid becomes double and quadruple, the quantity of zinc sulphate increases steadily from 0.65cc to 0.7cc to 0.75cc; of cadmium sulphate increases from 0.6 to 0.7 to 0.75 cc. This is opposed to Burton and Bishop's rule. In the case of magnesium sulphate, however, as the concentration of the sol becomes double, the quantity of the electrolyte first decreases from 0.8 to 0.6, and then increases slightly from 0.6 to 0.65 as the concentration of the sol becomes 4 times.

In the case of the trivalent electrolytes as the concentration of the colloid increases the quantities of electrolytes, necessary for coagulation also increase. Thus as the conc. of the colloid changes from A/2, to A and 2A, the quantities of sodium citrate increase from 3.2 to 3.75 to 6cc and of ferricyanide increases from 3.5 to 4.2 to 6.3cc, i.e., becomes practically double of the initial volume.

Table VIII shows clearly that Burton and Bishop's rule for a divalent electrolyte does not hold in the case of ferric hydroxide sol. As the concentration of the ferric hydroxide sol becomes 8 times and the quantity of potassium oxalate, becomes double. The increase in the volume of the electrolyte, potassium oxalate with increased concentration of the colloid is seen from the following curves Figs. 4-6.



Figs. 4, 5 and 6.

If we plot similar curves in the case of trivalent ions we find that the portions marked *abc* in Figs. 4, 5, and 6, show considerable similarity.

Thus in the case of ferric hydroxide sol, the volumes of both divalent and trivalent electrolytes increase with increasing concentration of the colloid.

The behaviour of alkali in precipitating colloidal $Fe(OH)_3$ is abnormal. Thus 0.5 cc of N/3.4 KOH can coagulate 5 cc of $Fe(OH)_3$ which will be coagulated by 2.5 cc of 2N KNO_3, and is thus about 35 times more active than potassium nitrate. As the sol becomes more dilute the quantity of KOH increases gradually. It might be interesting to note that a similar abnormal behaviour has been in the case of manganese dioxide sol (loc cit), alkali being far more active than many other electrolytes.

The precipitating power of HCl is similar to the precipitating power of other univalent electrolytes and this behaviour is quite normal.

An examination of Table IX shows the interesting fact that the undialysed ferric hydroxide sol wants larger volumes of electrolytes for its coagulation than the dialysed sol. In the case of the electrolyte KNO_3 the undialysed sol requires practically double of what the dialysed sol of the same concentration requires for its coagulation. Similar behaviour was observed in the case of colloidal managanese dioxide. Dialysis rendered the sol very unstable[1].

One possible explanation of the above behaviour in the case of positive $Fe(OH)_3$ is that small quantities of hydrochloric acid might have a peptising influencing over ferric hydroxide, the removal of which by dialysis makes the sol less stable.

It is desirable at this stage to compare, in general terms, the properties of this negatively charged ferric hydroxide sol with those of the positively charged sol. In the case of the positively charged sol, the coagulating ion is the anion, and from Freundlich's researches[2] it appears that the order of the precipitating anions is $Cr_2O_7 > SO_4 >$ OH > salicylate > benzoate > formate > $Cl > NO_3 > Br >$ I. From the work of Linder and Picton[3] the series appears to be $SO_4 > NO_3 > Cl > I > Br$. From our work on the positive sol the following series is obtained:—ferricyanide > citrate > oxalate > sulphate > hydroxide > nitrate > chloride. With the negative sol, the series is Br > KCNS > I > Cl > SO_4. Thus it will be seen that by reversing the charge on the colloid, the order of the precipitating ions has been reversed. A similar instance is known in the case of albumin, Hofmeister[4] has shown that the order of precipitation of proteids by anions of the same cation is citrate > tartrate > sulphate > acetate > chloride > NO_3 > I > CNS, whereas Posternak[5] and Pauli[6] have shown that the series is reversed if the experiments are carried in slightly acid solution. Bancroft's[7] observations in this connection are interesting: "Albumin is a specially interesting case because it is peptised readily by cations or anions. When it is negatively charged, as in a slightly alkaline solution, a strongly adsorbed anion will make it more negative and more stable. Consequently precipitation by a sodium salt will be more effective, the less readily the anion is adsorbed. On the other hand, in acid solution the sodium salt with the most strongly adsorbed anion will be the most effective in causing precipitation. Negatively charged albumin is precipitated readily by sodium chloride and

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[1] Ganguly and Dhar: loc. cit.
[2] Freundlich: Kapillarchemie, 352, 358 (1909).
[3] J. Chem. Soc. 87, 1926 (1905).
[4] Archiv. experim. Pathol. Pharmakol. 24, 247: 25, 1 (1889).
[5] Ann. de l'institut Pasteur, 15, 85ff (1901).
[6] Hofmeister's Beiträge, Z. Chem. Physiol. Pathol. 5, 27 (1903).
[7] "Applied Colloid Chemistry" 219 (1921).

not at all by sodium iodide, while positively charged albumin is precipitated by sodium iodide much more readily than by sodium chloride. Potassium iodide has more effect than potassium chloride with Rhodamine B, while the reverse is true with wool violet S". The experiments in this paper also reveal similar interesting facts. Thus potassium iodide has a greater effect on the negative sol than potassium chloride, whereas ,according to Linder and Picton, the reverse is true in the case of positive sol. Strontium chloride has a greater coagulative power on the positive sol than barium chloride, while in the case of the negative sol, barium chloride has a greater effect than the strontium salt. A similar effect is also to be observed in the case of potassium sulphate and zinc sulphate. The former has a greater coagulative power in the case of the positive sol, whilst the reverse is true in the case of the negative sol.

From the foregoing experimental results with antimony sulphide sol, it is seen that for univalent electrolytes like sodium chloride and lithium chloride with the gradual decrease of the concentration of the sol the quantity of electrolyte required for coagulation of a fixed volume of the sol in the specified time, gradually increases. In fact as the concentration of the sol in halved, the quantity of sodium chloride required for coagulation increases from 0.85 to 1.4 cc.

For divalent electrolytes, with the gradual increase of the concentration of the sol, the quantity of electrolyte required for coagulation remains fairly constant. Thus in the case of $Ba(NO_3)_2$, as the concentration of the colloid becomes twice and four times the original concentration, the quantity of $Ba(NO_3)_2$ required for coagulation changed from 0.5cc to 0.45cc. There is, however, discernible a tendency for the quantities of several divalent electrolytes to increase with the increase of concentration of the sol. In the case of lead, this effect is at its maximum. As the concentration of the sol increases from one gram to four grams of antimony potassium tartrate , the quantity of lead nitrate also increases from 0.6cc to 1.2cc, i.e., it actually becomes double as the concentration of the colloid is quadrupled. Another peculiarity was observed in the case of lead nitrate. The colloid would get precipitated immediately on the addition of lead nitrate. If a smaller amount of the electrolyte be added only a portion of the colloid will be precipitated, and will settle, whilst the liquid will remain coloured for several days. In other words, it was found that 0.6 cc of N/100 lead nitrate will precipitate completely 5 cc of the sol (1 gram per litre strength) in the course of a few minutes. When less than 0.6cc. of the electrolyte are added with a view to bringing the period taken for coagulation to about four hours, it was seen that immediately on the addition of the electrolyte a portion of the sol was coagulated, whilst a portion kept stable for days, as was indicated by the clear red colour of the liquid in the supernatant liquid after the precipitate had settled. The time factor seems to be very nearly absent in the case of lead nitrate.

For trivalent electrolytes, the quantity of electrolyte required for coagulation increases as the concentration of the colloid increases.

The following Table shows conclusively that with thorium nitrate and Sb_2S_3 sol, the greater the concentration of the sol the greater is the amount of electrolyte necessary for coagulation

Strength of Sol	Quantity of electrolyte necessary for coagulation
A	0.57 cc
$\frac{A}{2}$	0.325 cc
$\frac{A}{4}$	0.225 cc
$\frac{A}{8}$	0.15 cc
$\frac{A}{32}$	0.125 cc

In the case of quadrivalent thorium nitrate it has been seen that as the concentration of the colloid increases, the amount of electrolyte required for the coagulation of a fixed volume of the sol also increases. In fact as the concentration of the colloid becomes quadrupled the quantity of electrolyte increases from .225 to .575 cc is about 2.5 times as much.

The very large volume of electrolyte required for coagulation in the caes of the quadrivalent electrolyte thorium nitrate is rather remarkable. The thorium ion seems to form a complex with tartaric acid and its salts, hence its influence as a coagulating agent is appreciably decreased.

As has been said in the introductory part, time has a distinct ageing effect on antimony sulphide sol as will be evident from the following experimental results

Strength of the Sol	Date	Volume of electrolyte (NaCl) necessary for coagulation
2 grs antimony Pot. tartrate per litre	(1) Sept. 11	0.85 cc
	(2) Oct. 15	0.70 cc

Thus within a period of one month the sol has aged to such an extent as to require about 8% less of the electrolyte for its coagulation.

General Discussion

Let us try to visualise the mechanism of the coagulation of colloids by electrolytes. We shall consider the case of antimony sulphide sol, which is negatively charged. If we add say potassium nitrate to the sol, the negatively charged sol will attract and adsorb the potassium ions. The charge on the sol will be neutralised and one of the factors of the stability of the sol is removed. The Brownian movement of the particles, which is unaffected by electric charge, should keep the particles in suspension, provided the particles are not very near each other. Ordinarily, the particles of the colloid, being very near each other, collide violently and coalesce and settle down on neutralisation of the electric charge on them.

The negative ion (nitrate) will not be attracted by the negatively charged sol, but the phenomenon of adsorption which is not purely electrical in origin but is partly chemical in nature, might be effective and the colloid may be stabilised by the adsorption of the negative ions. But, as a matter of fact, as coagulation actually takes place on the addition of potassium nitrate to antimony sulphide, we infer that potassium ion is preferentially adsorbed in comparison with nitrate ions by the sol.

From our experiments on the direct adsorption of ions by hydrated manganese dioxide which is negatively charged, we have shown that the amount of electrolyte adsorbed is directly proportional to the quantity of manganese dioxide. It has also been proved that only a small percentage of the positive ions from the electrolytes is adsorbed.

A certain amount, which is very small, of the negative ion is also adsorbed by hydrated manganese oxide. The major portion of the electrolyte added remains unadsorbed.

It seems reasonable, therefore, that the greater the concentration of the sol, the greater should be the amount of electrolyte necessary to coagulate the sol, because the adsorbent is in greater quantity in the concentrated sols than in the dilute ones, provided the amount of charge and the size of the particles do not change on dilution.

From the foregoing experimental results, it will be seen that in the majority of cases, the greater the concentration of the sol, the greater is the amount of electrolyte necessary for coagulation. This will be found to be true irrespective of the nature of the sol and the valency of the precipitating ion, except with certain univalent salts, the cases of which will be discussed later on. This is true with NH_4Cl, KBr, KCl, KCNS, HCl, $HgCl_2$ $CeCl_3$, $MnSO_4$, $UO_2(NO_3)_2$, and $Al_2(SO_4)_3$ in the case of negatively charged ferric hydroxide sol; in other words with these electrolytes, the greater the concentration of the sol, the greater is the amount of the electrolyte added. With KI, NaCl, K_2SO_4, NaOH, $AgNO_3$, $SrCl_2$, and $ZnSO_4$, it will be found that by doubling the concentration of the sol, the amount of electrolyte necessary for coagulation is greater than that required for the diluted sol. In this case, practically all the electrolytes irrespective of their valencies support the conclusions arrived at above.

With positively charged ferric hydroxide sol it will be observed that greater quantities of the following electrolytes are necessary for coagulation with concentrated sols than with dilute ones:—$K_2C_2O_4$, $ZnSO_4$, $CdSO_4$, $MgSO_4$, alum, sodium citrate and $K_3Fe(CN)_6$.

In the case of antimony sulphide sol, our conclusion is verified with $Co(NO_3)_2$, $Ni(NO_3)_2$ $SrCl_2$, $ZnSO_4$, $Pb(NO_3)_2$, $Al(NO_3)_3$, $UO_2(NO_3)_2$, and $Th(NO_3)_4$,

With negatively charged manganese dioxide sol in general greater quantities of the following electrolytes are necessary for coagulation of concentrated sol than the dilute ones:—
KNO_3, KI, $KClO_3$, KCl, $KrSO_4$, sodium citrate, NaCl, NH_4Cl, $Ag(NO_3)$, $CuCl_2$, $CuSO_4$, $CaCl_2$, $SrCl_2$, $BaCl_2$, $AlCl_3$, $Cd(NO_3)_2$, $Co(NO_3)_2$ $Pb(NO_3)_2$, $ZnSO_4$, $HgCl_2$, and $K_3Fe(CN)_6$.

Now let us consider the work of other investigators Mukherjee and Sen[1] have studied the coagulating effects of LiCl, $Th(NO_3)_4$, $BaCl_2$ and $Al_2(SO_4)_3$ on arsenious sulphide sol. It will be observed from their results that greater quantities of $Al_2(SO_4)_3$, $Th(NO_3)_4$ and $BaCl_2$ (in very dilute solutions) are necessary for coagulation of concentrated sols than the dilute ones.

Similar conclusions could be drawn from Kruyt and Spek's researches[2] with barium and aluminium chlorides. Of the ions studied by the above authors only potassium ion has been found to be an exception to the rules enunciated in this paper.

From the results obtained by Burton and his coworkers our conclusion is verified with $BaCl_2$, $AlCl_3$, lanthanum sulphate, cerium nitrate, and zirconium chloride.

The researches of Murphy and Mathews[3] on the coagulation of ferric hydroxide sol by electrolytes show that the limiting concentration of electrolytes decrease markedly with decrease in the concentration of the sol in case of chloride, chromate, and ferricyanide ions. These results are in perfect harmony with the rule advanced in this paper.

From the point of view put forward in this article it is difficult to reconcile the results obtained by Mukherji and Sen and by Burton and his colleagues with univalent salts like KCl, LiCl etc. on the coagulation of arsenious sulphide mercuric sulphide, mastic and copper sols. They find that greater the dilution of the sol, the greater is the amount of electrolyte of the type of KCl necessary for coagulation.

There are certainly several factors controlling the process of coagulation. One set of factors is particularly important when we are considering univalent ions, whilst another set is powerful in the case of polyvalent ions. In the case of univalent ions, the concentration of electrolyte necessary is much greater than that necessary for polyvalent ions.

In considering the precipitating power of an univalent ion we have to take into account an equivalent quantity of another ion of equal or greater valency in a comparatively strong solution, whilst in dealing with trivalent ions, there is present in equivalent concentration another ion having less valency than the precipitating ion in comparatively feeble concentration.

As has been already said, it seems very likely that the univalent ion charged similarly to the sol should exert peptising influence on the sol and hinder its precipitation. This peptising effect of the similarly charged ion

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[1] J. Chem. Soc. 115, 461 (1919).

[2] Kolloid-Z. 25, 1 (1919).

[3] Science, 53, 581 (1921).

will be more evident, the more dilute the sol with which the coagulation experiments are carried on. This seems to be the explanation of the peculiar results obtained by the above investigators with univalent ions.

The view in this paper is in harmony with the theoretical results of Smoluchowski[1] on the phenomenon of coagulation of sols by electrolytes.

Smoluchowski assumes that the particles, when sufficiently near each other attract one another in consequence of the capillary forces, but that combination does not take place, under ordinary conditions in sols, is to be attributed to the protective effect of the electric double layer of the particles. When an electrolyte is added, a partial or complete discharge of the double layer takes place, owing to the adsorption of ions. The protective effect is diminished and from a certain concentration it does not suffice to prevent the particles from joining together. Still another influence must be taken into consideration, it causes the collision of the particles, but at the same time checks their permanent combination viz., the molecular forces, which among other things, manifest themselves in the Brownian movement.

Freundlich[2] assumes that the partially discharged particles in a slowly coagulating colloid, do not join together unless their power of colliding with each other exceeds a minimum value. If the violence of collision is of decisive importance for the coagulation, not only the relative velocity of the particles, but also their mass should have some influence on the progress of coagulation.

In order to explain the anomalous behaviour of univalent ions on the coagulation of sols, Mukherjee and Sen have considered that dilution increases the distance between the particles of a sol. The increased distance somehow decreases the facility for coalescence and thus increases its stability. The outline of the phenomenon of coagulation as sketched in the foregoing pages being the accepted view of the process, it becomes difficult to understand the influence of electrolytes on the greater or less distance between the individual particles. Because the main function of the ions is to remove the electrical double layer and the ions are not contemplated to take any part in the process of coalescence which follows later on, after once the double layer is removed.

Again there is another difficulty with regard to the factor of distance between the individual particles. Smoluchowski from theoretical reasoning has come to the conclusion that the coagulation curves obtained from the different concentrations series of the colloid and the electrolyte must be similar. Moreover, the phenomenon of coagulation of sols by different electrolytes is more or less identical in nature. Consequently if we accept the explanation of Mukherjee and Sen for univalent ions based on the difference in the distance of the individual particles we ought to expect the same behaviour with polyvalent ions. Actually, however, the behaviour of polyvalent ions is very different from that of few univalent ions, which are really only exceptional cases.

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[1] Kolloid-Z. 21, 98 (1917); compare Westgren and Reitstötter: J. Phys. Chem. 26, 535 (1922).

[2] Kolloid-Z. 23, 163 (1918).

It is clear from what has already been said that the simple explanation of the behaviour of ions irrespective of their valencies, on the coagulation of sols of varied concentrations, based on the ordinary conceptions of adsorption, is quite, adequate at least, qualitatively, for most of the experimental work done in this line.

Summary of Conclusion

The majority of electrolytes investigated by us in the cases of negatively and positively charged ferric hydroxide sols, negatively charged managnese dioxide sol and antimony sulphide sol of different concentrations follow the simple rule that the greater the concentration of the sol, the greater is the concentration of the electrolyte necessary for coagulation irrespective of the valency of the precipitating ions. The results obtained by Murphy and Mathews are in complete harmony with the above rule.

The majority of electrolytes investigated by Burton and his colleagues, by Mukherjee and Sen, and by Kruyt and coworkers with different sols at various concentrations support the rule enunciated in this paper.

Consequently we venture to remark that the "so-called" generalisations of Burton and coworkers are not real generalisations, but are based on some exceptional cases and should be modified in view of our experimental work and of the simple rule, enunciated in this paper, explaining satisfactorily the greater amount of experimental work actually available. The rule stands on accepted views about adsorption.

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Allahabad: May 7, 1923.

THE BEHAVIOR OF SILVER IODIDE IN THE PHOTO-VOLTAIC CELL

BY ALLEN GARRISON*

Becquerel[1] was the first to observe that the photo-potential of the silver iodide electrode: electrolyte cell was not always positive. He coated silver with the halide by direct action of the vapors of the halogen and placed the electrode thus formed in an electrolyte. He studied the effect of light on this system by comparing its potential with that of a similar electrode which was kept in the dark. If the silver iodide coating was not too thick on the electrode he found that the photo-potential was always positive, that is the light caused the electrode to take a positive charge from the liquid. But when the coating had reached a critical thickness there appeared a negative light effect which was only temporary and was ordinarily followed by the positive effect.

Minchin[2] observed similar effects with several cells but regarded the negative effect as exceptional and it has even been stated by more recent investigators that the light effect is always positive in the case of silver electrodes prepared in this way[3].

In the case of the cuprous oxide photo-voltaic cell it was formerly thought that the photo-potential was always positive but it has recently been demonstrated that the potential induced by the light may be either positive or negative depending on the condition of the electrode and the nature of the electrolyte.[4] Therefore the phenomenon differs from the Hallwachs-Lenard or photo-electric effect in that the direction of the change in potential has not the same significance.

It is the purpose of this report to present the experiments which show a remarkable similarity between the action of the silver halides and cuprous oxide. The same general theory applies to both, the conditions which determine both the nature and the direction of the light effects being almost identical. The results are of interest in photography because they furnish new data on the photo-chemical behavior of the silver halides.

Experimental Procedure

The light-sensitive electrodes were prepared either by the direct action of the vapors of the halide or by electrochemical deposition of a thin layer of the silver halide on a polished silver electrode. The electrochemical method produced a more uniform coating and the thickness could be controlled more accurately than by the direct action of the vapors, but the same results can be obtained with electrodes prepared by either method.

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[1] Becquerel: La Lumière, 2, 129 (1868).

[2] Minchin: Phil. Mag. 31, 207 (1891).

[3] Wildermann: Phil. Trans. 206A, 335 (1906).

[4] Garrison: J. Phys. Chem. 27, 601 (192)3.

The electrodes were made of thin sheet silver about 3 cm in length and 2 cm in width. They were always coated on the back with paraffin so that only the front surface which was exposed to the light was in electrical contact with the electrolyte.

The electrolyte was always saturated with silver iodide. This fixed the product of the silver and iodine ions but their ratio could be set at any desired value by making up the solution with the proper concentration of potassium iodide or silver nitrate as the case demanded.

The electrode and electrolyte were placed in a rectangular glass vessel which was painted with black paint on all sides but one. The electrode was fixed facing the transparent side and close to it so that the light had to traverse only 0.5 cm of the electrolyte before falling on the electrode. A 0.10 N. calomel half-cell completed the photo-voltaic cell.

The cell was mounted in a light-proof box having a single rectangular window for the admittance of light to the sensitive electrode. The window was covered with a water screen 2 cm in thickness. To measure the light intensity a thermopile was mounted in the box with the photo-voltaic cell as close as possible to the sensitive silver electrode. A moving coil galvanometer was used to measure the current from the thermopile, the deflections being taken as a measure of the light intensity. The e.m.f. of the photo-voltaic cell, that is the potential difference between the silver electrode and the mercury of the calomel half-cell was measured with a high grade potentiometer of standard make. This was the reversible voltage of the cell, since no polarizing current was permitted to pass.

A 500 c.p. tungsten filament lamp was used as a light source. When the effect of various intensities of white light was investigated it was necessary to have the same spectral distribution of energy for each intensity since the different colors do not have the same effect. For this reason the intensity could not be varied by changing the temperature of the source and any partial screening method was not desirable. The light source was placed behind a large lense at a distance from it less than its focal length so that a diverging cone of light was produced. The solid angle of the cone was varied by a slight change in the distance from the lense to the light and thus the intensity of the light over a small area at the center of the cone was varied without any appreciable change in the spectral distribution of energy. Light from the center of this cone was passed through the window of the box containing the photo-voltaic cell and thermopile.

Experimental Results

The conditions which determine the sign of the photo-potential. There are two factors which determine the sign of the charge which the electrode receives in light. The first is the thickness or density of the silver iodide over the electrode. If all the other conditions such as the light intensity and color and the constitution of the electrolyte remain constant then the photo-potential may be made to be either positive or negative by changing the thickness of the silver iodide coating.

This was demonstrated experimentally by starting with a polished silver electrode and coating it with several successive thin layers of silver iodide observing the light effect under fixed conditions after each successive layer of the halide. The results are given in Table I.

TABLE I
The Influence of the Thickness of the Silver Iodide

No.	$EA_{Ag\rightarrow Cal.}$	dE (−)	dE (+)	E_2
1	−0.4327	none	trace	−0.4327
2	−0.4315	none	+0.0015	−0.4320
3	−0.4296	none	+0.0031	−0.4300
4	−0.4275	trace	+0.0031	−0.4282
5	−0.4273	−0.0005	+0.0032	−0.4280
6	−0.4270	−0.0012	+0.0030	−0.4280

The first determination was made with a polished silver electrode in 0.1 normal potassium iodide solution saturated with silver iodide. The electrode was then removed and a thin coating of iodide applied by the electrochemical method. Thus electrode No. 2 had one coating and No. 3 two, etc. Each time the coating was thickened by the additional layer of the halide.

In column 1 are the original potentials relative to the 0.1 N calomel electrode in the dark. In columns 2 and 3 are the negative and positive photo-potentials E(−) and E(+) respectively and in column 4 the potential to which the electrode returned in the dark after illumination.

It will be noticed that the positive photo-potential was very small when the electrode had only a small amount of iodide on it and that the effect reached a maximum only after the third coating. Up to this point the light effect was entirely positive. When the fourth layer was applied a slight negative effect appeared which increased in magnitude with each additional coating. The negative effect was similar to that of the cuprous oxide electrode, that is the electrode became negative when the light was first turned on but if illumination was continued at constant intensity the negative charge disappeared and was followed by the positive effect.

From the first column it may be seen that the original potential of the electrode in the dark increased with each additional layer of the silver iodide. After six layers the potential had increased 5.7 millivolts. The constitution of the electrolyte had not altered during the measurements, the solution remained saturated with silver iodide and therefore the concentration of the silver and iodine ions was the same for each determination. The change in potential of the electrode must therefore be attributed to some change in the nature of the silver electrode. The direction of the shift in potential would demand that the solution pressure of the silver be decreased, that is the tendency of the silver to ionize decreases as the surface becomes thickly coated with the iodide. This is equivalent to a dilution or decrease in the active concentration of the silver. This has been found to occur in the case of copper also.

After an electrode had been illuminated it did not return to its original dark potential as may be seen from column 4 but had always shifted toward the original dark potential of electrode No. 1, that is −0.4327. This indicates that a partial destruction of the layer of iodide had occurred during the illumination thus increasing the concentration of the silver.

This increase in the solution pressure of the silver was accompanied by a decrease in the negative photo-potential. Electrode No. 6 behaved like electrodes Nos. 3 or 4 after the first illumination had partly destroyed the iodide coating and the dark potential increased to −0.4280. This will presently be shown quantitatively.

The negative light effects may be made larger and less transient by decreasing the concentration of the potassium iodide in the solution. This brings us to the second factor which influences the direction of the light effect: the photo-potential may be made to be either positive or negative by varying the ratio of the silver to the iodine ions in the saturated silver iodide solution.

The experimental demonstration of this is recorded in Table II. The same electrode was used in the first eleven observations. It was coated with a moderately thick layer of the halide corresponding approximately to electrode No. 3 in Table I. Electrodes having thicker coatings were also used as indicated in the table. The last corresponded in thickness to No. 6 in Table I. Almost any thickness of coating may be used to observe the effect of various electrolytes but with thin coatings the negative effect is usually only temporary and it is difficult to get large positive effects with very thick coatings on the first exposure to light.

TABLE II

The Influence of the Ratio of Silver to Iodine Ions

$T = 27°$

$E_{Ag \rightarrow Hg}$	C_{Ag+}	C_{I^-}	dE
−0.2705	0.757×10^{-12}	1.42×10^{-4}	−.0030
−0.2400	2.42 ”	.412 ”	−.0085
−0.2200	5.24 ”	.190 ”	−.0140
−0.2120	7.07 ”	.141 ”	−.0160
−0.2050	10.7 ”	.093 ”	−.0262
	(2) Iodine Ions increased (KI added)		
−0.2330	3.16 ”	.316 ”	−.0125
−0.3200	.112 ”	8.91 ”	+.0023
−0.3320	.0707 ”	14.1 ”	+.0032
	(3) Silver Ions increased ($AgNO_3$ added)		
−0.2332	3.16 ”	.316 ”	−.0036
−0.1771	27.1 ”	.0368 ”	−.0124
−0.1560	61.0 ”	.0164 ”	−.0120
	(4) Thicker Coating used and $AgNO_3$ added		
−0.2201	5.24 ”	.190 ”	−.0195
−0.1889	17.4 ”	.0575 ”	−.0261
	(5) Very Thick Coating used and $AgNO_3$ added		
−0.4270	1.86×10^{-14}	.0547	−.001 +.003
−0.3455	4.22 ”	.0023	−.0260

The electrode was first placed in dilute Na_2SO_4 solution saturated with AgI. Its potential relative to the 0.1 N calomel electrode in the dark before each exposure to light is recorded in the first column and the photo-potential with its proper sigh, positive or negative, in the fourth column. After each observation a little $AgNO_3$ or KI was added to the solution as is indicated thus changing the ratio of the concentrations of the silver and iodide ions. This change can be calculated from the electrode potential. The silver ion concentration in moles per liter corresponding to each electrode potential is recorded in column 2 and the corresponding iodine ion concentration in column 3. The solubility of silver iodide was taken as 1.0×10^{-8} moles per liter[1] and the dissociation considered complete at this dilution.

From the first five observations it may be seen that the negative effect increases with increasing ratio of silver to iodine ions. The positive effect was developed by reversing the process and adding potassium iodide to the solution. This could be repeated as often as desired.

Parts 4 and 5 show that a smaller concentration of silver ions is required to develop the positive effect the thicker the coating. This is to be expected from the results of Table I. The reverse is also true, it requires a larger concentration of silver ions to develop the negative effect in the case of electrodes having thin coatings of halide.

The same electrode was used for parts 1, 2 and 3 of Table II; but it will be noticed that the negative photo-potentials in part 3 are smaller than the ones in part 1 for the same silver ion concentration and even for much larger concentrations. This is another example of the destructive action of the light on the silver iodide coating. This decomposition is more pronounced the larger the concentration of the silver ions and is thus larger the larger the negative effect.

The photo-chemical decomposition of the silver iodide coating. The halide coating when first formed was yellow white in color. When it was placed in potassium iodide solution and illuminated it remained practically unchanged in color and properties. In silver nitrate solution however where the photo-potential was negative the coating was rapidly darkened by the light and its properties changed. Its equilibrium potential in the dark was reduced, that is less positive, and it was found to behave like an electrode having a thinner coating when illuminated a second time.

In case the coating was relatively thin the reversal of light effect took place rapidly and both a negative and a positive effect were observed on illumination, the negative effect appearing first as it did in the cuprous oxide cells. On second illumination the negative effect was usually found to have been destroyed and only the positive effect remained.

The decomposition was greatest on electrodes which had large negative photo-potentials and which were in a solution containing a high concentration of silver ions. In the case of electrodes with thick coatings in solutions where

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[1] Hill: J. Am. Chem. Soc. 30, 68 (1908).

the silver ions were reduced negative effects could be obtained which were more permanent. There was practicallv no recoil in the positive direction in this case the photo-chemical decomposition being retarded. This was the type of electrode which was used to measure the influence of light intensity on the negative effect. Even under these conditions there was a slight darkening in light and the negative effect was reduced after long exposure.

The extent of the decomposition for some electrodes is shown in Table III.

TABLE III

The Photo-chemical Decomposition of the Coating

E(dark)	dE	E_2 (dark)	dE_2
−0.2369	−0.0065	−0.2415	+0.0025
−0.2388	−0.0055	−0.2436	+0.0026
−0.2405	−0.0020	−0.2430	−0.0006
Thick Coating and Small C_{Ag^+}			
−0.3450	−0.0260	−0.3455	−0.0240
Thin Coating and Small C_{Ag^+}			
−0.3457	+0.0025	−0.3456	+0.0025
−0.3600	+0.0028	−0.3602	+0.0028

The potential in the dark of each electrode is recorded in column 1 and the effect of the first illumination in column 2. After strong illumination the dark potential was again observed and recorded in the third column and the result of a second illumination in the fourth column. The first three observations were made on electrodes having moderately dense coatings in such a strength of silver ions that the decomposition was rapid. It will be noticed that where the decomposition is most pronounced as indicated by the change in dark potential, the negative effect was greatly reduced. Electrodes which had been darkened in light could be returned to their original condition by the action of the vapors of iodine or by electrochemical coating in potassium iodide solution.

The relation between the photo-potential and the intensity of the illumination. The measurements of the positive photo-potentials in Table IV were made with a silver electrode covered with a moderately thick film of the iodide and placed in a 0.01 normal KI solution. Measurements were made on several different electrodes in order to find the conditions which gave the largest and most uniform positive effects. It has already been pointed out that electrodes having very thin films of the iodide did not have large positive effects. The most satisfactory results were obtained with films as thick as it was possible to use without developing the negative effect.

The relation between the negative effect and the light intensity is shown in Table V. Due to the unstable character of a dense coating of the iodide the results were not as uniform as those for the positive effect, for it was shown that photo-chemical decomposition is most rapid when the negative effect is largest. The best results were obtained with a very thick film of iodide on the electrode and a comparatively small silver ion concentration. Larger negative potentials were obtained in solutions more concentrated in silver ions but decomposition was too rapid to compare relative light intensities. Observations were made as quickly as possible to insure the constancy of the electrode.

TABLE IV

The Relation between Light Intensity and the Positive Photo-potential

$E_{Ag \rightarrow Hg}$	dE	I (intensity)
−0.3542	+.0110	23.1
−0.3550	+.0095	18.0
−0.3551	+.0082	13.5
−0.3545	+.0066	9.2
−0.3551	+.0048	6.0
−0.3549	+.0049	5.4
−0.3551	+.0040	4.1
−0.3549	+.0036	3.5
−0.3549	+.0028	2.4
−0.3551	+.0024	2.2
−0.3549	+.0023	1.75

TABLE V

The Relation between Light Intensity and the Negative Photo-potential

$E_{Ag \rightarrow Hg}$	dE	I (intensity)
−0.1887	−.0290	14.0
−0.1896	−.0272	11.9
−0.1886	−.0234	9.5
−0.1886	−.0195	6.5
−0.1887	−.0180	5.5
−0.1887	−.0134	3.2
−0.1889	−.0087	1.5

The first column in each table contains the electrode potentials in the dark compared with the 0.1 normal calomel cell. The observations were not made in the order of their appearance in the table but those having the smallest dark potentials were made first. During the course of the observations the potential of the electrode in the dark shifted from −0.3554 to −0.3551 in Table IV and from −0.1886 to −0.1896 in Table V. The order of the observations can easily be picked out.

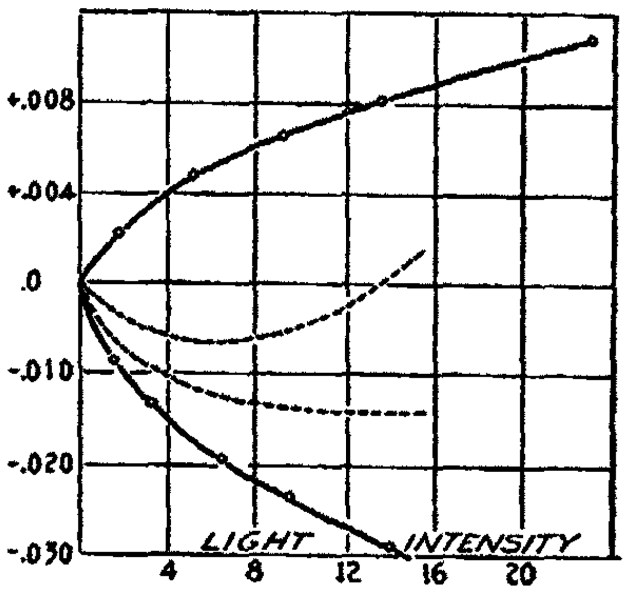

Fig. 1

The changes in potential on illumination (dE) are recorded in the second column and the light intensity (I) in the third column. The methods of changing and measuring the light intensity have already been described.

A good idea of the relation between the photo-potential and the light intensity can be gotten from Fig. 1. The upper curve was plotted with the positive photo-potentials and the lower curve with the negative photo-potentials against the light intensity on the X-axis. While the negative values are larger than the positive ones for the same intensity of illumination the curves were found to be of the same form, for when the changes in the pressure of the ions were calculated and the reciprocal of these values plotted against the reciprocal of the light intensities, the points fell along straight lines within the limits of the experimental error. The approximate relation can thus be expressed by the equation

$$\frac{1}{n} = \text{constant} \cdot \frac{1}{I} + \text{constant} \qquad (1)$$

for both the positive and the negative effects.

The dotted curves are drawn in Figure 1 to show the behavior of an electrode which was placed in a solution containing such a silver ion pressure that it developed the negative potential first on illumination but the maximum potential was not maintained on constant illumination. The lower curve gives the value of the maximum negative photo-potential for each intensity and the upper curve gives the potential to which the electrode returned after constant illumination for five minutes. For example when illuminated with light of intensity 15 the electrode first became negative to about −0.0150 volts but after five minutes constant illumination lost the negative charge and rose to approximately +0.0010 volts.

The cuprous oxide electrodes were found to have these same properties in relation to the light intensity except that cuprous oxide electrodes have not yet been made which have the negative effect without the positive recoil as was obtained with silver iodide. Results corresponding to the upper curve and to the two dotted curves have been obtained with cuprous oxide. (Garrison: Loc. cit.)

The relation between the color of the light and the photo-potential. While the data on this point are at present limited, enough is known to say that here also there is a marked difference between the photo-voltaic effect and the well known photo-electric effect. There does not appear to be a simple relation between the photo-potential and the frequency but a complicated one depending on the nature of the substance on the electrode.

The results in Table VI were obtained by admitting the light into the box containing the photo-voltaic cell and thermopile after passing it through different color filters. The approximate range of wave-lengths admitted by each filter are given in the first column. The light intensity was adjusted to the

TABLE VI

The Influence of the Color of the Light

Color	Range in microns.	Intensity	dE
Red	.81 − .65	5	.0008
R Y	.80 − .53	5	.0008
R Y G	.80 − .52	5	.0011
O G	.68 − .50	5	.0012
Y G	.55 − .49	5	.0007
G B V	.50 − .39	2	.0029

same intensity behind each ray filter (column 2) with the exception of the blue violet where the energy was not sufficient. The positive photo-potential developed in each color was placed in the third column.

This is strongly suggestive of the range of sensibility of the silver iodide photographic plate, the effect being greater in the blue and violet with a slight maximum in the yellow green. It is of interest to note in this connection that a silver iodide electrode when dyed in eosine developed larger photo-potentials in the longer wave-lengths just as the photographic plate becomes more sensitive to the red and yellow after a similar treatment. A more quantitative investigation of the influence of the optical and chemical sensitizers is being continued.

Theoretical Part

Since there is such a distinct similarity between the behavior of silver iodide and cuprous oxide in the photo-voltaic cells it is reasonable to conclude that the same general theory may be applied to both substances. It is the purpose of this discussion to show that this may be done and that it furnishes a simple explanation of the photo-chemical properties of silver iodide.

The theory which was suggested for the cuprous oxide cells was based on the assumption that the light tends to separate the cuprous ions from the oxygen ions thus increasing the solubility product of the oxide.

Silver iodide is soluble in water to the extent of 1.0×10^{-8} moles per liter. Thus in a saturated solution of silver iodide both silver and iodine ions are present to the extent that their product is 1.0×10^{-16}. If we suppose that the solid halide is more soluble in light then, on illumination, the product of the ions can exceed the value 1.0×10^{-16} by an amount which depends on the light intensity and color.

When both the ions are present in the same amount (1.10^{-8} moles each), we would expect them to increase in approximately the same proportion in light.

When the solution contains potassium iodide such that the iodine ions have a concentration of 0.01 moles per liter the concentration of the silver ions are reduced to 1.0×10^{-14} in the dark. In the light the iodine ions would remain practically fixed in number because of their relatively large amount while the silver ions would increase until the new solubility product was reached. For it requires far less decomposition to double the silver ions for example to 2.0×10^{-14} than to double the iodine ions to 0.01.

The reverse would be true if the silver ions had a concentration of 0.01 moles per liter and the iodine ions $1.0 \times 10-_{14}$ for in this case the iodine ions would be formed in the light and the silver ions remain fixed.

A silver electrode whose potential is determined by the reaction

$$Ag \rightleftarrows Ag^+ + (-)$$

may be used to measure the increase in silver ion concentration in the solution when illuminated. It would thus become positive on illumination. From the preceding discussion it is evident that this positive photo-potential would increase with increasing potassium iodide concentration.

On the other hand an iodine electrode capable of the equilibrium

$$I_2 \rightleftarrows 2\ I^- + 2\ (+)$$

may be used in the solution to measure the concentration of the iodine ions. It would become negative on illumination and the maximum changes I^- ion concentration would be obtained in a solution containing silver nitrate.

The electrode we are considering is the silver electrode coated with a layer of solid silver iodide. It is possible for this electrode to behave either as a reversible silver electrode or as a reversible iodine electrode. Thus the two factors which were found to determine the direction of the photo-potential of this electrode are the factors which determine whether the electrode will behave as a silver electrode or as an iodine electrode and also the extent of the change in the concentration of the ion considered.

From the electro-chemical standpoint an electrode can be in equilibrium with an electrolyte only after all the ions in the electrolyte capable of an equilibrium have set up that equilibrium at the electrode. The electrode we are considering when placed in potassium iodide solution cannot be regarded as a silver electrode any more than it can be considered as an iodine electrode, a hydrogen electrode, an oxygen electrode and a potassium electrode. Each substance and the corresponding ion must have pressures determined by the well known expression

$$\text{E.P.} = E_{\text{normal}} \pm \frac{RT}{nF} \ln \frac{P_{\text{ion}}}{P} \qquad (2)$$

and therefore we may write

$$\text{E.P.} = E_{Ag} + k \ln \frac{P_{Ag^+}}{P_{Ag}} = E_{I_2} - k \ln \frac{P_{I^-}}{P_{I_2}} = E_{H_2} + k \ln \frac{P_{H^+}}{P_{H_2}} \qquad (3)$$

When the electrode is illuminated we suppose that either or both the silver and iodine ions increase in number so that the problem resolves itself into a determination of the reaction which really determines E.P. and which reaction is determined by the value of E.P. This was considered at some length in the paper on the cuprous oxide cells so that an outline of the conclusions is all that is necessary here.

1. At an electrode where several ionic reactions are in equilibrium, a "primary" electro-chemical reaction is one which can be displaced reversibly an appreciable amount at constant electrode potential, (reactants at constant pressure). And a "secondary" electro-chemical reaction is one which can be displaced reversibly an appreciable amount only as the electrode potential changes, (pressure of the reactants changes with the action).

2. It follows that, the "primary" reaction is displaced according to Faraday's law by a current which is passed through the electrode. In the absence of any "primary" reaction the one which resembles it most closely is displaced but only as the E.P. continually changes.

3. The "primary" reaction fixes the value of the electrode potential by equation (2) and the E.P. thus fixed determines the pressures of all the reactants of the "secondary" reactions by equation (3). In the absence of any "primary" reaction the one which resembles it most closely fixes the value of E.P.

In the case we are considering the reaction $Ag \rightleftarrows Ag^+ + (-)$ is the primary reaction as long as metallic silver and solid silver iodide are present. The reaction may be displaced at constant pressure since the solid silver iodide acts as a reservoir for silver ions. The iodine, hydrogen, oxygen and other reactions are secondary, their pressures being fixed by the primary reaction.

When the silver electrode is thickly covered with the halide the silver is no longer constant in amount. Its concentration may be reduced by making the film of halide thicker. Thus it was found that the electrode potential in the dark was more positive the thicker the coating (Table I). In this case the silver ion equilibrium is no longer primary.

The silver halide film and the solution about the electrode are able to absorb some iodine. They can thus act as a reservoir for iodine. When the silver equilibrium becomes secondary the iodine equilibrium $I_2 \rightleftarrows 2\,I^- + 2\,(+)$ resembles a primary reaction most closely and may determine the potential of the electrode.

From this consideration the positive photo-potential is to be expected when the coating is relatively thin and the iodine ion concentration relatively large. On the other hand the negative photo-potential is to be expected when the silver is cut off from the solution by a thick layer of the iodide and the silver ion concentration relatively large.

The photo-chemical decomposition of the halide may be traced to an electrochemical deposition of metallic silver. The decomposition was found to be greatest when the largest negative photo-potentials were developed in the presence of a high concentration of silver ions. It is obvious that these are just the conditions under which the silver ions would have the greatest tendency to deposit.

It has been known for a long time that silver iodide emulsion on the photographic plate is not sensitive to light when precipitated in an excess of potassium iodide solution. The plate may be sensitized by dipping in silver nitrate solution. While silver nitrate forms complexes with iodine the theory that this alone accounts for the sensitizing action of silver nitrate does not take into account the fact that potassium iodide also forms complexes with iodine and should also sensitize the plate, rather than retard its action.

If the photo-chemical decomposition is an electrochemical deposition as is suggested here, each particle of halide in the emulsion may be regarded as an electrode and it would be less stable in light when the conditions were such that it developed a negative photo-potential in the presence of excess silver ions. The conditions would be fulfilled by dipping the photographic plate in silver nitrate solution.

This theory may be harmonized with either the metallic particle theory or the solid solution theory of the latent image, both theories have already been suggested.[1] The silver may be deposited over the exposed area as very fine particles of metal or dissolved in the halide in the form of a solid solution.

When a layer of silver halide is thus decomposed by light the particles of silver give the electrode a dark color. After this has happened the reaction $Ag \rightleftarrows Ag^+ + (-)$ becomes primary once more and the electrode loses its negative photo-potential. This would also be accompanied by an increase in the negative electrode potential in the dark. This accounts for the changes represented in Table III.

The relation between light intensity and the photo-potential can be obtained from the Einstein photo-chemical law in the following way:

Since the number of quanta of any color of light is proportional to the intensity of radiation of that color, then the amount of decomposition may be put proportional to the intensity of illumination so long as all the active colors are changed in the same proportion. The reaction we are considering is a first order reaction so that the amount of decomposition may be proportional to the amount of silver iodide also.

Let N_o = the amount of AgI present in the dark. and n = the amount of Ag^+ formed by the light. and $N = N_o - n$ = the amount of AgI left at intensity I.

$$n = \text{constant} \cdot N \cdot I$$

$$= \frac{N_oI - nI}{k}$$

$$= \frac{N_oI}{(k + I)}$$

The values of N_o, N and n may be expressed in terms of concentration or moles per unit volume.

$$\text{then}\quad dE = \frac{RT}{vF}\ln\left(\frac{n+n_o}{n_o}\right) \qquad \text{where } n_o = P_{Ag} \text{ in dark}$$

$$\text{or}\quad dE = C \log\left(1 + \frac{n}{n_o}\right) \qquad \text{let } N_o' = \frac{N_o}{n_o}$$

$$\text{therefore } dE = C \log\left[\frac{N_o'I}{(k + I)} + 1\right]$$

(C) is a constant depending on the temperature and the valence of the ion. *k* is a constant depending on the nature of the substance and the illumination. It may also depend on the magnitude of N_o'. When *k* is small compared with

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[1] Sheppard and Wightman: Science 58, 89 (1923).

I, that is for very large values of I, dE approaches a constant. For very small values of I, dE approaches $_3$C log (const · I+1) and *n* becomes linear with I. The general relation is expressed in equation (1), that is $\frac{1}{n}$ is linear with $\frac{1}{I}$.

The experimental results are not accurate enough over a wide range to test the theory closely and get the exact values of N° and *k*, but it is interesting to note that the approximate relation can be obtained from the simple theory.

The same calculation can be applied to the negative photo-potential where (n) represents the amount of iodine ions liberated in the light and (n°) the amount in the dark at equilibrium.

Goldmann[1] has suggested a theory for the photo-voltaic cell based upon the Hallwachs-Lenard effect or photo-emission of electrons and Sheppard and Wightman (loc. cit.) advanced a similar theory for the photographic plate. If this idea is accepted it is difficult to see how the negative photo-potential can be formed under the conditions described above and bear the same relation to the light intensity as the positive effect. This would require that the solid particle of silver or halide develop a negative charge by the emission of a negative electron. The phenomena may be explained however by the theory that the primary effect of the light is a separation of the charged elements as ions.

Summary

Silver iodide photo-voltaic cells have been made which have both positive and negative photo-potentials. The sign of the photo-potential was found to depend on the thickness of the silver iodide layer over the electrode and on the ratio of the concentration of silver ions to that of iodine ions in the electrolyte.

The relation between the light intensity and the changes in electrode potential were measured for both the positive and the negative effects.

Decomposition of the silver halide was found to occur during the maximum negative effects in the presence of a high concentration of silver ions.

The results are in agreement with the theory that the silver iodide becomes more soluble in light. The relation between light intensity and photo-potential has been obtained with the aid of this theory.

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[1] Goldmann: Ann. Physik. (4) **44**, 901 (1914).

ADSORPTIVE CAPACITY OF WOOD CHARCOAL FOR DISSOLVED SUBSTANCES, IN RELATION TO THE TEMPERATURE OF CARBONISATION

BY JAMES C. PHILIP AND JOHN JARMAN

In recent years much attention has been devoted to the preparation of active charcoals, and to the study of the conditions favourable to activation. Partly owing to the great variety of sources from which charcoal can be obtained, and partly because the final product, being an indefinite material cannot be reproduced with certainty, the views of independent workers on the significance of different relevant factors are by no means in agreement. Among the points on which the recorded evidence is conflicting are (1) the optimum temperature conditions for the production of an active charcoal, and (2) the question whether, of a number of charcoals, the one which is found to have the highest adsorptive activity in regard to a particular adsorbed substance is necessarily also the most active in relation to other substances. The present communication embodies the results of experiments designed to throw light on these points.

The general procedure adopted was to carbonise a selected wood by keeping it for known periods at definite temperatures. The resulting product was analysed for carbon, hydrogen, and ash, and then, without further heat treatment, its adsorptive capacity was determined in relation to a variety of dissolved substances.

Experimental

Birch wood was employed throughout, and for the purpose of carbonisation was cut into small 1/4" cubes. These were packed into a wide glass or quartz tube, and the latter, roughly plugged with asbestos, was inserted in an electrically heated oven previously raised to the desired temperature. After a definite period the current was switched off, and the oven was allowed to cool. The charcoal was ground roughly by hand and then in a mechanically driven agate mortar for about twenty minutes.

For the purpose of combustion, which in each case was carried out in duplicate, the charcoal was dried for two hours in the steam oven, and during the subsequent cooling and weighing was exposed to the air for the shortest possible time. The treatment of the charcoals and the procedure followed in their combustion were uniform throughout, and were adopted after much preliminary work. The percentage of ash in the charcoals was at first deduced from the residue in the platinum boat, but later was estimated by incinerating 5 grams of the material in a platinum crucible.

In all, 25 charcoals were prepared and analysed, and the details of their preparation and composition are given in Table I.

TABLE I

No. of Sample	Temp. of carbonisation	Duration of carbonisation	Carbon %	Hydrogen %	Ash %	Atomic Ratio C/H
1	350°C	2 hours	76.03	3.98	1.54	1.6
2	"	4 "	77.67	3.86	1.54	1.7
3	"	6 "	77.93	3.49	1.80	1.9
4	"	10 "	83.24	3.21	1.64	2.2
5	"	18 "	83.69	3.02	1.65	2.3
6	"	24 "	85.19	3.34	1.96	2.1
7	450°C	4 "	89.74	2.96	1.42	2.5
8	"	6 "	90.54	2.83	1.43	2.7
9	"	9 "	90.61	2.80	1.46	2.7
10	550°C	4 "	93.27	2.05	1.43	3.8
11	"	6 "	93.50	1.94	1.46	4.0
12	650°C	4 "	94.73	1.18	1.86	6.7
13	"	6 "	95.06	0.91	1.86	8.7
14	750°C	4 "	95.52	0.55	1.62	14.5
15	"	6 "	95.86	0.52	1.58	15.4
16	850°C	4 "	96.34	0.39	1.32	20.6
17	"	6 "	96.52	0.34	1.30	23.7
18	450°C	6 "	91.37	2.72	1.66	2.8
19	"	6 "	91.81	2.75	1.46	2.8
20	"	6 "	91.43	2.74	0.97	2.8
21	"	6 "	91.54	2.54	1.46	3.0
22	"	6 "	90.38	2.28	2.44	3.3
23	850°C	6 "	91.97	0.73	4.25	10.5
24	"	6 "	92.84	0.74	4.01	10.4
25	"	6 "	96.36	0.37	1.38	21.7

In Table I, besides details as to the temperature and duration of carbonisation, and figures for the percentage of carbon hydrogen and ash, there are included values of the atomic ratio C/H. So long as the facility for access of air is kept uniform, a condition observed in the preparation of Samples 1-19 and 25, these values show a regular progression with the temperature at which carbonisation was carried out. For a given temperature the value of the ratio rises in almost every case with increase in the duration of carbonisation. These results are in general agreement with such similar observations and measurements on wood charcoal as have been put on record (for example, Violette: Ann. chim. phys., **32**, 322 (1851)).

The question how far the charcoals can be reproduced by carbonisation at a given temperature and with as nearly as possible the same conditions in respect to access of air, is answered by reference to Nos. 18 and 19, which are duplicates of No. 8, and to No. 25, which is a duplicate of No. 17. The degree of reproducibility is fairly good in these cases.

The charcoals Nos. 20-24 are not strictly comparable with the others, since the conditions as regards access of air were somewhat different. In the preparation of Nos. 20-22 at 450° air had freer access, and in increasing degree, to the vessel in which the carbonisation was carried out. Still more was this the case with Nos. 23 and 24 prepared at 850°, and the difference in the conditions of carbonisation is reflected in the high percentage of ash and in the low value for the C/H ratio compared with that obtained for No. 17 or No. 15. A high value for the ash is to be expected when there is increased facility for oxidation, but the difficulty of securing entirely reproducible results is shown by the fact that No. 24, (in the preparation of which the facility for oxidation was judged to be the greater) has a somewhat lower ash content than No. 23. Of the charcoals Nos. 20-22, prepared at 450°, the last has a distinctly high ash content, corresponding with the fact that the facility for air access was greatest in that case, but, on the other hand, the low figure found for the ash of No. 20 is puzzling when compared with the fairly steady values found for Nos. 1-19. The exceptional character of Nos. 23 and 24, brought out by the analytical results, is demonstrated also, as shown below, by their adsorptive capacities.

Each of the charcoals detailed in Table I was tested in regard to its power of removing dissolved substances from solution. Aqueous solutions of five substances, of different character, were employed in the tests, which consisted in shaking up one gram of the charcoal, mechanically for a definite period in each case, with a standard quantity of the solution, and determining the final concentration of the latter. This was found by well-known analytical methods in the cases of iodine, oxalic acid, and methylene blue, and polarimetrically in the cases of tartar emetic and quinine sulphate.

In connexion with the question of reproducibility, it is interesting to note from the results recorded in Table II that charcoals 18 and 19, which were designedly prepared as duplicates of No. 8 (see p.000 and Table I) are found to have also nearly the same adsorptive capacity. A similar remark applies to Nos. 17 and 25.

When the figures for samples 1-19 and 25 (all prepared under more or less uniform conditions so far as access of air was concerned) are examined, it is seen that in the tests with tartar emetic and quinine sulphate there is, apart from minor fluctuations, a steady improvement in adsorptive capacity with rise of the temperature of carbonisation. In the case of methylene blue the charcoals prepared at 650° and below appear to be of approximately equal activity, while those prepared at 850° (or even at 750°) exhibit a marked rise in adsorptive power. With iodine and oxalic acid as reference substances, on the other hand, there is a general rise in the adsorptive value (not very marked in the case of iodine) to a maximum for the charcoals prepared at 650°. Those prepared at 750° and 850° exhibit a definite falling off in activity, so far as the adsorption of iodine or oxalic acid is concerned.

TABLE II

Showing percentages of dissolved substances removed from a standard quantity of its aqueous solution by 1 gram of the different charcoals.

No. of Sample	Iodine	Oxalic Acid	Methylene Blue	Tartar Emetic	Quinine Sulphate
1	34.3	2.8	7.9	0.04	0.2
2	33.8	2.4	8.4	0.08	0.2
3	31.2	3.2	8.1	0.07	0.3
4	31.7	6.5	8.7	0.08	0.4
5	29.3	4.4	10.8	0.08	0.3
6	29.1	6.3	11.1	0.04	0.4
7	36.6	9.6	8.9	0.3	0.7
8	37.8	10.4	9.4	0.3	0.7
9	38.0	10.5	8.7	0.4	0.8
10	39.6	13.6	8.4	0.3	2.2
11	40.5	16.0	7.9	0.9	2.3
12	40.4	18.6	7.8	0.8	2.8
13	42.5	21.3	9.6	1.8	2.8
14	26.1	11.6	11.0	3.0	5.2
15	27.2	12.6	25.9	2.9	5.4
16	13.7	7.2	27.7	3.3	5.7
17	10.7	8.3	27.9	3.3	5.8
18	39.4	11.5	7.8	0.4	0.7
19	39.7	11.7	7.9	0.4	0.8
20	38.9	11.5	8.1	0.4	0.8
21	38.8	11.5	9.2	0.3	0.7
22	36.8	14.5	8.5	0.3	0.7
23	37.7	21.5	36.3	6.8	10.0
24	48.2	24.9	56.8	7.6	27.9
25	10.7	8.6	27.4	3.3	5.8

The effect of prolonging the carbonisation at a given temperature does not, from these experiments, appear to be very pronounced; in some cases there is an increase in adsorptive power, but it is not very regular, and in one instance the figures show a fairly definite decrease.

A very notable increase of activity is exhibited by those charcoals prepared at 850° with comparatively free access of air (Nos. 23 and 24). The adsorptive power of these specimens is, by comparison, remarkably high, notably in relation to methylene blue, tartar emetic, and quinine sulphate.

Summary

(1) Birch wood has been carbonised at a series of regulated temperatures and for definite periods.

(2) Twenty-five samples of charcoal so obtained have been analysed for carbon, hydrogen, and ash, and their adsorptive power has been tested in relation to iodine, oxalic acid, methylene blue, tartar emetic and quinine sulphate.

(3) It appears that the optimum temperature for the production of an active charcoal by carbonisation alone varies with the nature of the substance in the adsorption of which the charcoal is to be used.

(4) Increased facility for access of air during the carbonisation results, at the higher temperatures, in a marked rise of activity.

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NEWTON AND THE PEACOCK[1]

BY WILDER D. BANCROFT

When I was in Montreal last autumn, Professor Eve called my attention to a copy of the first edition of Newton's Opticks published in 1704 and owned by the Department of Physics in which there is a passage on the colors of peacock's feathers. Professor Eve was good enough to send me a typewritten transcript of this passage; but I have decided to put in some other paragraphs from Newton's Opticks and shall consequently make use of the third edition published in 1721, of which Cornell has a copy.

On p. 168 Newton says that "it has been observed by others that transparent substances, as glass, water, air, etc., when made very thin by being blown into bubbles, or otherwise formed into plates, do exhibit various colours according to their various thinness, although at a greater they appear very clear and colourless." He then discusses experiments with glass prisms, plates, and lenses pressed together so as to form what are now known as Newton's rings.

"Compressing two prisms hard together that their sides (which by chance were a very little convex) might somewhere touch one another: I found the place in which they touched to be absolutely transparent, as if they had there been one continued piece of glass. For when the light fell so obliquely on the air, which in other places was between them, as to be reflected, it seemed in that place of contact to be wholly transmitted, insomuch that when looked upon, it appeared like a black or dark spot, by reason that little or no sensible light was reflected from thence, as from other places; and when looked through it seemed (as it were) a hole in that air which was formed into a thin plate, by being compressed between the glasses. And through this hole objects which were beyond might be seen distinctly, which could not at all be seen through other parts of the glasses where the air was interjacent."

Better results were obtained by pressing together a plano-convex lens for a fourteen-foot telescope and a large double convex lens for about a fifty-foot telescope, p. 173. "Next to the pellucid central spot made by the contact of the glasses succeeded blue, white, yellow, and red. The blue was so little in quantity that I could not discern it in the circles made by the prisms, nor could I distinguish any violet in it, but the yellow and red were pretty copious, and seemed about as much in extent as the white, and four or five times more than the blue. The next circuit in order of color immediately encompassing these were violet, blue, green, yellow, and red: and these were all of them copious and vivid, excepting the green which was very little in quantity, and

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[1] This paper is a necessary consequence of experiments supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

seemed much more faint and dilute than the other colours. Of the other four, the violet was the least in extent, and the blue less than the yellow or red. The third circuit or order was purple, blue, green, yellow, and red; in which the purple seemed more reddish than the violet in the former circuit, and the green was much more conspicuous, being as brisk and copious as any of the other colours, except the yellow; but the red began to be a little faded, inclining very much to purple. After this succeeded the fourth circuit of green and red. The green was very copious and lively, inclining on the one side to blue and on the other side to yellow. But in this fourth circuit there was neither violet, blue, nor yellow, and the red was very imperfect and dirty. Also the succeeding colours became more and more imperfect and dilute, till after three or four revolutions they ended in perfect whiteness." When the glasses were most compressed so as to make the black spot appear in the center, the colours reckoned in order from the center were: black, blue, white, yellow, red; violet, blue, green, yellow, red; purple, blue, green, yellow, red; greenish blue, red; greenish blue, pale red; greenish blue, reddish white.

On p. 187 Newton says: "The precedent observations were made with a rarer thin medium terminated by a denser, such as was air or water, compressed between two glasses. In those that follow are set down the appearances of a denser medium thin'd within a rarer, such as are plates of muscovy glass, bubbles of water, and some other thin substances terminated on all sides with air.

"If a bubble be blown with water first made tenacious by dissolving a little soap in it, 'tis a common observation, that after a while it will appear tinged with a great variety of colours. To defend these bubbles from being agitated by the external air (whereby their colours are irregularly moved one among another, so that no accurate observation can be made of them) as soon as I had blown any of them I cover'd it with a clear glass, and by that means its colours emerged in a very regular order, like so many concentrick rings encompassing the top of the bubble. And as the bubble grew thinner by the continual subsiding of the water, these rings dilated slowly and overspread the whole bubble, descending in order to the bottom of it, where they vanish'd successively. In the mean while, after all the colours were emerged at the top, there grew in the center of the rings a small round black spot, like that in the first observation, which continually dilated itself till it became sometimes more than 1/2 or 3/4 of an inch in breadth before the bubble broke. At first I thought there had been no light reflected from the water in that place, but observing it more curiously, I saw within it several smaller round spots, which appeared much blacker and darker than the rest, whereby I knew that there was some reflexion at the other places which were not so dark as those spots. And by farther tryal I found that I could see the images of somethings (as of a candle or the sun) very faintly reflected, not only from the great black spot, but also from the little darker spots which were within it.

"Besides the aforesaid colour'd rings there would often appear small spots of colours, ascending and descending up and down the sides of the bubble, by reason of some inequalities in the subsiding of the water. And sometimes small black spots generated at the sides would ascend up to the larger black spot at the top of the bubble, and unite with it.

"Because the colours of these bubbles were more extended and lively than those of the air thinn'd between two glasses, and so more easy to be distinguish'd, I shall here give you a farther description of their order, as they were observ'd in viewing them by reflexion of the skies when of a white colour, whilst a black substance was placed behind the bubble. And they were these; red, blue; red, blue; red, blue; red, green; red, yellow, green, blue, purple, red, yellow, green blue, violet; red, yellow, white, blue, black.

"The three first successions of red and blue were very dilute and dirty, especially the first, where the red seem'd in a manner to be white. Among these there was scarce any other colour sensible besides red and blue, only the blues (and principally the second blue) inclined a little to green.

"The fourth red was also dilute and dirty, but not so much as the former three; after that succeeded little or no yellow, but a copious green, which at first inclined a little to yellow, and then became a pretty brisk and good willow green, and afterwards changed to a blueish colour; but there succeeded neither blue nor violet.

"The fifth red at first inclined very much to purple, and afterwards became more bright and brisk, but yet not very pure. This was succeeded with a very bright and intense yellow, which was but little in quantity, and soon chang'd to green: But that green was copious and something more pure and lively, than the former green. After that follow'd an excellent blue of a bright sky-colour, and then a purple, which was less in quantity than the blue, and much inclined to red.

"The sixth red was at first of a very fair and lively scarlet, and soon after of a brighter colour, being very pure and brisk, and the best of all the reds. Then after a lively orange follow'd an intense bright and copious yellow, which was also the best of all the yellows, and this changed first to a greenish yellow, and then to a greenish blue; but the green between the yellow and the blue, was very little and dilute, seeming rather a greenish white than a green. The blue which succeeded became very good, and of a very fair bright sky-colour, but yet something inferior to the former blue; and the violet was intense and deep with little or no redness in it. And less in quantity than the blue.

In the last red appeared a tincture of scarlet next to violet, which soon became changed to a brighter colour, inclining to an orange; and the yellow which follow'd was at first pretty good and lively, but afterwards it grew more dilute, until by degrees it ended in perfect whiteness. And this whiteness, if the water was very tenacious and well temper'd, would slowly spread and dilate it self over the greater part of the bubble; continually growing paler at the top, where at length it would crack in many places, and those cracks, as they dilated, would appear of a pretty good, but yet obscure and dark sky-colour; the white between the blue spots diminishing, until it resembled the threds of an irregular net-work, and soon after vanish'd and left all the upper part of the bubble of the said dark blue colour. And this colour, after the aforesaid manner, dilated it self downwards, until sometimes it hath overspread the whole bubble. In the mean while at the top, which was of a darker blue than the bottom, and appear'd also full of many round blue spots, something darker than the rest, there would emerge one or more very black spots, and within those, other spots of an intenser blackness, which I mention'd in the former observation, and these continually dilated themselves until the bubble broke.

"If the water was not very tenacious the black spots would break forth in the white, without any sensible intervention of the blue. And sometimes they would break forth within the precedent yellow, or red, or perhaps within the blue of the second order, before the intermediate colours had time to display themselves.

"By this description you may perceive how great an affinity these colours have with those of air described in the fourth observation, although set down in a contrary order, by reason that they begin to appear when the bubble is thickest and are most conveniently reckon'd from the lowest and thickest part of the bubble upwards."

Newton has also considered the colors by transmitted light, pp. 181, 194. "By looking through the two contiguous object glasses, I found that the interjacent air exhibited rings of colours, as well by transmitting light as by reflecting it. The central spot was now white, and from it the order of the colours were: yellowish red; black, violet, blue, white, yellow, red; violet, blue, green, yellow, red, etc. But these colours were very faint and dilute, unless when the light was trajected very obliquely through the glasses: for by that means they became pretty vivid. Only the first yellowish red, like the blue in the fourth observation, was so little and faint as scarcely to be discern'd. Comparing the colour'd rings made by reflexion, with these made by transmission of the light; I found that white was opposite to black, red to blue, yellow to violet, and green to a compound of red and violet. That is, those parts of the glass were black when looked through, which when looked upon appear'd white, and on the contrary. And so those which in one case exhibited blue, did in the other case exhibit red. And the like of the other colours. . .

"As in the ninth observation [preceding paragraph], so here, the bubble, by transmitted light, appear'd of a contrary colour to that which it exhibited by reflexion. Thus when the bubble being look'd on by the light of the clouds reflected from it, seem'd red at its apparent circumference, if the clouds at the same time, or immediately after, were viewed through it, the colour at its circumference would be blue. And, on the contrary, when by reflected light it appeared blue, it would appear red by transmitted light. . . .

"A thin transparent body, which is denser than its ambient medium, exhibits more brisk and vivid colours than that which is so much rarer; as I have particularly observed in the air and glass. For blowing glass very thin at a lamp furnace, those plates encompassed with air did exhibit colours much more vivid than those of air made thin between two glasses."

The question of the peacock is brought in under Proposition V of the Second Book, p. 226. "The transparent parts of bodies according to their several sizes reflect rays of one colour and transmit those of another, on the same grounds that thin plates or bubbles so reflect or transmit those rays. And this I take to be the ground of all their colours.

"For if a thinn'd or plated body, which being of an even thickness, appears all over of one uniform colour, should be slit into threds, or broken into fragments, of the same thickness with the plate; I see no reason why every thred or fragment should not keep its colour, and by consequence why a heap of those threds or fragments should not constitute a mass or powder of the same colour, which the plate exhibited before it was broken. And the parts of all natural bodies being broken like so many fragments of a plate, must on the same grounds exhibit the same colours.

"Now that they do so, will appear by the affinity of their properties. The finely colour'd feathers of some birds, and particularly those of the peacocks tails, do in the very same part of the feather appear of several colours in several positions of the eye, after the very same manner that thin plates were found to do in the 7th and 19th observations, and therefore their colours arise from the thinness of the transparent parts of the feathers; that is, from the slenderness of the very fine hairs, or *capillamenta*, which grow out of the sides of the grosser lateral branches or fibres of those feathers. And to the same purpose it is, that the webs of some spiders by being spun very fine have appeared colour'd as some have observed, and that the colour'd fibres of some silks by varying the position of the eye do vary their colour."

While it is very interesting that Newton should have hit on the true explanation of the colors in peacock's feathers, his opinion on this subject does not carry any special weight because the question of surface reflection did not come up seriously until the discovery of such dyes as magenta in the nineteenth century, and because Newton used the explanation of thin films in a number of cases in which we now know that that explanation was inapplicable.

Newton apparently believed that all colors are the colors of thin films, pp. 227, 230. "By mixing divers liquors very odd and remarkable productions and changes of colours may be effected, of which no cause could be more obvious and rational than that the saline corpuscles of one liquor do variously act upon or unite with the tinging corpuscles of another, so as to make them swell, or shrink (whereby not only their bulk but their density also may be changed) or to divide them into smaller corpuscles, (whereby a colour'd liquor may become transparent) or to make many of them associate into one cluster, whereby two transparent liquors may compose a colour'd one. For we see how apt those saline menstruums are to penetrate and dissolve substances to which they are applied, and some of them to precipitate what others dissolve."

"Scarlets, and other reds, oranges and yellows, if they be pure and intense are most probably of the second order. Those of the first and third order also may be pretty good, only the yellow of the first order is faint, and the orange and red of the third order have a great mixture of violet and blue.

"There may be good greens of the fourth order, but the purest are of the third. And of this order the green of all vegetables seem to be, partly by reason of the intenseness of their colours, and partly because when they wither some of them turn to a greenish yellow, and others to a more perfect yellow or orange, or perhaps to red, passing first through all the aforesaid intermediate colours. Which changes seem to be effected by the exhaling of the moisture which may leave the tinging corpuscles more dense, and something augmented by the accretion of the oily and earthy part of that moisture. Now the green without doubt is of the same order with those colours into which it changeth, because the changes are gradual, and those colours, though usually not very full, yet are often too full and lively to be of the fourth order.

"Blues and purples may be either of the second or third order, but the best are of the third. Thus the colour of violets seems to be of that order, because their syrup by acid liquors turns red, and by urinous and alcalizate turns green. For since it is of the nature of acids to dissolve or attenuate, and of alcalies to precipitate or incrassate, if the purple colour of the syrup was of the second order, an acid liquor by attenuating its tinging corpuscles would change it to a red of the first order, and an alcali by incrassating them would change it to a green of the second order; which red and green, especially the green, seem too imperfect to be the colours produced by these changes. But if the said purple be supposed of the third order, its change to red of the second, and green of the third, may without any inconvenience be allow'd.

"If there be found any body of a deeper and less reddish purple than that of the violets, its colour most probably is of the second order. But yet there being no body commonly known whose colour is constantly more deep than theirs, I have made use of their name to denote the deepest and least reddish purples, such as manifestly transcend their colour in purity.

"The blue of the first order, though very faint and little, may possibly be the colour of some substances; and particularly the azure colour of the skies seems to be of this order. For all vapours when they begin to condense and coalesce into small parcels, become first of that bigness whereby such an azure must be reflected before they can constitute clouds of other colours. And so this being the first colour which vapours begin to reflect, it ought to be the colour of the finest and most transparent skies in which vapours are not arrived to that grossness requisite to reflect other colours, as we find it is by experience.

"Whiteness, if most intense and luminous, is that of the first order, if less strong and luminous a mixture of the colours of several orders. Of this last kind is the whiteness of froth, paper, linen, and most white substances: of the former I reckon that of white metals to be. For whilst the densest of metals, gold, if foliated, is transparent, and all metals become transparent if dissolved in menstruums or vitrified, the opacity of white metals ariseth not from their density alone. They being less dense than gold would be more transparent than it, did not some other cause concur with their density to make them opake. And this cause I take to be such a bigness of their particles as fits them to reflect the white of the first order. For if they be of other thicknesses they may reflect other colours, as is manifested by the colours which appear upon hot steel in tempering it, and sometimes upon the surface of melted metals in the skin or scoria which arises upon them in their cooling. And as the white of the first order is the strongest which can be made by plates of transparent substances, so it ought to be stronger in the denser substances of metals than in the rarer of air, water, and glass. Nor do I see but that metallic substances of such a thickness as may fit them to reflect the white of the first order, may, by reason of their great density (according to the tenour of the first of these propositions) reflect all the light incident upon them, and so be as apake and splendent as it's possible for any body to be. Gold, or copper mix'd with less than half their weight of silver, or tin, or regulus of antimony, in fusion, or amalgamed with a very little mercury, become white; which shews both that the particles of white metals have much more superficies, and so are smaller than those of gold and copper, and also that they are so opake as not to suffer the particles of gold or copper to shine through them. Now it is scarce to be doubted, but that the colours of gold and copper are of the second or third order, and therefore the particles of white metals cannot be much bigger than is requisite to make them reflect the white of the first order. The volatility of mercury argues that they are not much bigger, nor may they be much less, lest they lose their opacity, and become either transparent as they do when attenuated by vitrification, or by solution in menstruums, or black as they do when ground smaller, by rubbing silver, or tin, or lead, upon other substances to draw black lines. The first and only colour which white metals take by grinding their particles smaller, is black, and therefore their white ought to be that which borders upon the black spot in the center of the rings of colours, that is, the white of the first order. But if you would hence gather the bigness of metallic particles, you must allow for their density. For were mercury transparent, its density is such that the sine of incidence upon it (by any computation) would be to the sine of its refraction, as 71 to 20, or 7 to 2. And therefore the thickness of its particles, that they may exhibit the same colours with those of bubbles of water, ought to be less than the thickness of the skin of those bubbles in the proportion of 2 to 7. Whence it's possible that the particles of mercury may be as little as the particles of some transparent and volatile fluids, and yet reflect the white of the first order.

"Lastly, for the production of black, the corpuscles must be less than any of those which exhibit colours. For at all greater sizes there is too much light reflected to constitute this colour. But if they be supposed a little less than is requisite to reflect the white and very faint blue of the first order, they will, according to the 4th, 8th, 17th and 18th observations, reflect so very little light as to appear intensly black, and yet may perhaps variously refract it to and fro within themselves so long, until it happen to be stifled and lost, by which means they will appear black in all positions of the eye without any transparency. And from hence may be understood why fire, and the more subtle dissolver putrefaction, by dividing the particles of substances, turn them to black, why small quantities of black substances impart their colour very freely and intently to other substances to which they are applied; the minute particles of these, by reason of their very great number, easily overspreading the gross particles of others; why glass ground very elaborately with sand on a copper plate, 'till it be well polish'd, makes the sand, together with what is worn off from the glass and copper, become very black: why black substances do soonest of all others become hot in the sun's light and burn, (which effect may proceed partly from the multitude of refractions in a little room, and partly from the easy commotion of so very small corpuscles;) and why blacks are usually a little inclined to a bluish colour. For that they are so may be seen by illuminating white paper by light reflected from black substances. For the paper will usually appear of a bluish white; and the reason is, that black borders on the obscure blue of the first order described in the 18th observation, and therefore reflects more rays of that colour than of any other.

"In these descriptions I have been the more particular, because it is not impossible but that microscopes may at length be improved to the discovery of the particles of bodies on which their colours depend, if they are not already in some measure arrived to that degree of perfection. For if those instruments are or can be so far improved as with sufficient distinctness to represent objects five or six hundred times bigger than at a foot distance they appear to our naked eyes, I should hope that we might be able to discover some of the greatest of those corpuscles. And by one that would magnify three or four thousand times perhaps they might all be discover'd, but those which produce blackness. In the mean while I see nothing material in this discourse that may rationally be doubted of, excepting this position. That transparent corpuscles of the same thickness and density with a plate, do exhibit the same colour. And this I would have understood not without some latitude, as well because those corpuscles may be of irregular figures, and many rays must be obliquely incident on them, and to have a shorter way through them than the length of their diameters, as because the straitness of the medium pent in on all sides within such corpuscles may a little alter its motions or other qualities on which the reflexion depends. But yet I cannot much suspect the last, because I have observed of some small plates of muscovy glass which were of an even thickness, that through a microscope they have appeared of the same colour at their edges and corners where the included medium was terminated. which they appeared of in other places. However it will add much to our satisfaction, if those corpuscles can be discovered with microscopes; which if we shall at length attain to, I fear it will be the utmost improvement of this sense. For it seems impossible to see the more secret and noble works of nature within the corpuscles by reason of their transparency.—"

Newton does not admit the existence of what are now called pigment colors. He considers all forms of color as structural color. One does not quite understand his point of view because most of the colors of plants are not different by transmitted and reflected lights. In the case of the blue sky, we are dealing with a structural color due to very fine particles; but the principle involved is not that of interference.

There can be no question as to Sir Isaac's meaning because he repeats his views with great clearness, p. 251. "I have hitherto explained the power of bodies to reflect and refract, and shew'd, that thin transparent plates, fibres and particles do, according to their several thicknesses and densities, reflect several sorts of rays, and thereby appear of several colours, and by consequence that nothing more is requisite for producing all the colours of natural bodies than the several sizes and densities of their transparent particles."

THE FREEZING OF WATER IN CAPILLARY SYSTEMS: A CRITICAL DISCUSSION

BY E. A. FISHER

A considerable amount of work has been done at various times on the freezing of water in such capillary systems as inorganic hydrogels, soils, etc. This work has been mainly along two lines (a) the actual depression of the freezing point as related to the moisture content and nature of the system and (b) dilatometric determinations of the amounts of water that will freeze at various temperatures. Both lines of investigation have been applied by G. T. Bouyoucos and his co-workers[1] to soil-water systems with such remarkable results that to accept them at their face value would necessitate an entirely new conception of the moisture relations of the soil and the forms in which water exists in the soil and other similar capillary systems. Thus it was found by Bouyoucos that the lowering of the freezing point of a soil increased in approximately geometrical progression as the moisture content decreased in arithmetical progression and this seemed to indicate that, contrary to general belief, the concentration of the soil solution in any particular soil sample is not inversely proportional to the moisture content of the sample. The difficulty was explained away by assuming that a considerable proportion of the water of the soil was either physically adsorbed or loosely chemically combined or present in solid solution so that this portion of the water was not free to function as a solvent but was removed from its active liquid phase. A similar conclusion had been reached, apparently quite independently, by Foote and Saxton[2] in a dilatometric study of the freezing of water in sand, lampblack and the hydrogels of alumina, ferric oxide, and silica. These workers found that considerable quantities of water, in some cases up to 50 or 60 percent of the dry weight of gel, apparently failed to freeze in the hydrogels while no such phenomenon was observed with sand or lampblack.

Bouyoucos and his co-workers obtained similar results in their dilatometric studies on soils. They found in 73 cases examined that the amount of water that failed to freeze at 78°C was nothing in the case of quartz sand but varied with soils from 1.2% (calculated on a dry weight basis) with a coarse sand to 14.6% with a California silty clay loam. They also give the following

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[1] G. T. Bouyoucos and others: Mich. Agr. Coll. Expt. Sta. Tech. Bull. 24 (1915); 27 (1916); 31 (1916); 36 (1917); 37 (1917); 42 (1918); J. Agri. Res. 8, 195 (1917); 15, 331 (1918); 20, 267 (1920); 20, 587 (1921); Soils Sci. 11, 33, 255, (1921).

[2] J. Am. Chem. Soc. 38, 588 (1916); 39, 627, 1103 (1917).

for other materials: peat 6%, silica 32%, animal charcoal 19.0%, burned clay 2.8% and lampblack 2.0%.[1]

These conclusions have not been generally accepted by workers in soil science and some critical work has been done. Foote and Saxton found with silica gels that the amount of water that would not freeze at −78°C varied from 29.6% to 44.6%. Lenher[2] submitted samples of silica gel to pressure so as to squeeze out some of the water and found a water content of 12.3 to 12.9% after exposure for some time to a pressure of 272,700 kgs. per sq. in. In these experiments more than half the 'combined' water of Foote and Saxton was squeezed out by mechanical pressure. While these results are not theoretically inconsistent[3] with Foote and Saxton's conception of 'combined' water the amount of such water squeezed out by the pressure applied appears surprisingly large.

Keen[4] submitted the freezing point depression data of Bouyoucos to mathematical analysis and concluded that in any given soil sample the water rendered unfree is not a constant amount but must vary with the total moisture content a conclusion that was contradicted by later experimental work of Bouyoucos.[5]

F. W. Parker[6] showed that, although the presence of colloidal particles had been shown by many investigators to have an extremely small or even negligible effect on the freezing point of a liquid, very different results obtained if the amount of water is reduced until it is entirely in the film or capillary condition. Thus ferric oxide, alumina, soil, or silica would cause a depression of the freezing point of water, benzene, or nitrobenzene when the liquid exists in the film or capillary condition in the solid material. This had been shown to be the case by Bouyoucos himself[7] with quartz and water but he attributed it to the solubility of something in the sand itself. Parker pointed out that if part of the water is rendered unfree by a soil then aqueous solutions of alcohol, glycerin or sugar should be rendered more concentrated when added to a dry soil.[8] It was demonstrated that such was not the case and that the freezing point depression due to capillarity and that due to the presence of solutes are in all cases additive.[9] Parker's work appears to be satisfactory as

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[1] This may be experimental error since Foote and Saxton (loc. cit). found in one case with lampblack that 101.78% of the water froze at −78°C. The error with sand was +1.85%.

[2] J. Am. Chem. Soc. 43, 391 (1921).

[3] Nernst: "Theoretical Chemistry", 766 (1923); Roozeboom: "Die heterogenen Gleichgewichte," Erstes Heft, p. 213.

[4] J. Agri. Sci. 9, 400 (1919).

[5] Soil Sci. 11, 255 (1921).

[6] J. Am. Chem. Soc. 43, 1011 (1921).

[7] Bull. 24 and 31 loc. cit.

[8] This would be so even if the solutes were appreciably adsorbed by the dry soil. The amount of 'combined' water may be as much as 40 or 50 percent of the total water present. It is unlikely that a non-electrolyte would be adsorbed to a degree that would obliterate the effect on concentration of the removal of such large amounts of solvent. Sugar is known to be adsorbed but is so only to a slight extent.

[9] Soil Sci. 13, 43 (1922).

a qualitative basis for clearing up the apparent anomalies of the freezing point depressions but leaves the dilatometric results untouched. It is the object of the present note to indicate a few criticisms that may affect the validity of the conclusions drawn from the experimental results.

The work of Bouyoucos, Foote and Saxton, and of Parker establishes the fact that the freezing point of water in capillary systems is lower than that of water in bulk.[1] Thus in Fig. 1[2] are plotted the volumes of contraction and expansion upon cooling to 20°C and rewarming of quartz sand. AB represents the contraction on cooling the sand + water from 5° to −1°. At −1° freezing commenced, the whole of the water froze at this temperature and BC measures the increase in volume consequent on the freezing. From this measured expansion the amount of water frozen can be calculated and in the case of quartz sand corresponds to the known water content. CD measures the contraction on cooling the sand + ice from −1° to −20°. CD is almost exactly parallel to AB. On raising the temperature the process is quantitatively reversed except that melting did not take place until 0° was reached.

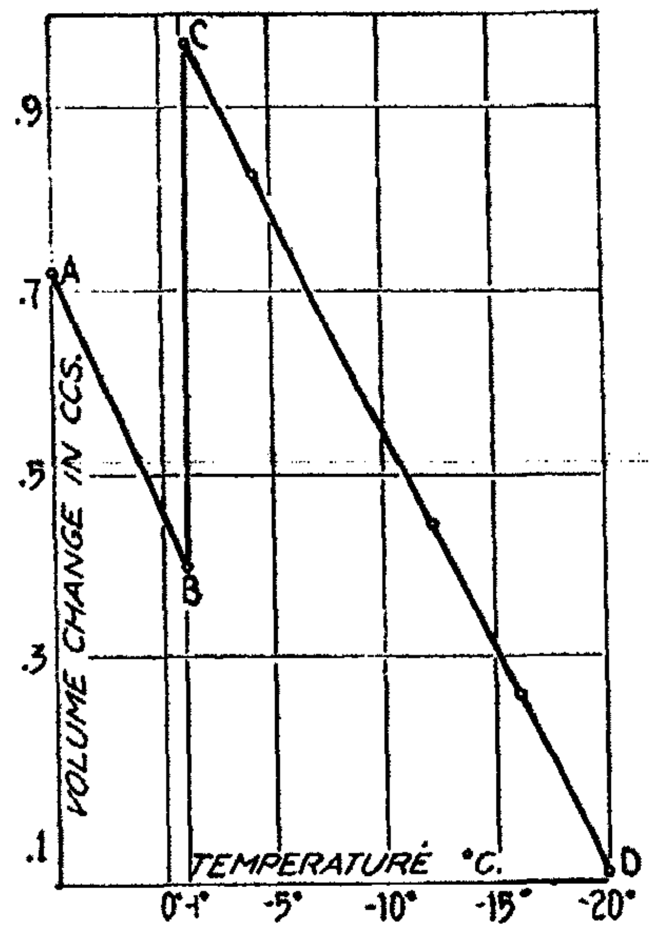

Fig. I

In Fig. 2 are given the data for a clay soil. Again AB represents the contraction of soil + water from 5° to −1°. DC measures the expansion due to the freezing of some water at −1°. Along CD from −1° to −4° the curve represents the result of expansion due to the freezing of capillary water and of the contraction of soil + ice + water due to decreasing temperature. From −4° to −78° the curve is straight within the limits of experimental error and is nearly parallel to AB. DE should be coincident with CD up to −4°. The slight divergence is probably due to some little water in the very finest capillaries not freezing until below −4° although the amount in this particular case is insufficient to produce a definite curvature.

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[1] A possible source of error in determinations of freezing point depressions of liquids in capillary systems may be pointed out here as no reference seems to have been made to it in the literature of the subject. If 100 gms. of soil containing 1.0 percent of water is supercooled to −4°C and then solidification is induced, 80 calories of (latent) heat are liberated. Of these about 4 Cal. are used up in raising the temperature of the ice from −4° to approximately 0°, leaving 67 cals. to raise the 99 gms. dry soil through the same temperature range. Assuming the specific heat of soil to be about 0.20 [H. E. Patten: U. S. Dept. Agri., Bur. Soils, Bull. 50, (1909); Bouyoucos: Mich. Agri. Coll. Expt. Sta., Tech. Bull. 17 (1913)], 79 cals. will be needed for the latter purpose. Hence measurements of F. P. D. in such systems are accurate only if the water content is greater than a certain critical amount, *e.g.* in the above example about 1.0 percent.

[2] Figs. 1 and 2 are reproduced from Bouyoucos: Bull. 36 loc. cit.

It has been suggested that some or all the apparent depression of the freezing point may be due to supercooling and Bouyoucos has shown that capillary water may be supercooled to −4.2° without freezing if agitation is carefully avoided. Water in bulk can be supercooled to −6° without freezing but in all cases supercooling is negligible if agitation is employed. Supercooling can however be definitely ruled out here since, on warming the frozen mass, ice begins to melt at −4°. A solid cannot be superheated above its melting point and the fact that curvature in DE begins at −4° shows that some ice must be melting at that temperature. With some samples of silica gel Foote and Saxton showed that curvature began on rewarming even below −30°. There can be no doubt therefore as to the experimental facts of capillary water having a lower F.P. than water in bulk. Such a lowering of F.P. must also follow theoretically from the lowering of vapor pressure of water due to capillarity since only the liquid phase is so affected[1]. That is, the vapor pressure-temperature curve for capillary water is below that of water in bulk while the curve for the ice phase is unaffected. Hence the point of intersection of the ice and water v.p. curve, *i.e.* the F.P. must be lower in capillary than in non-capillary systems.

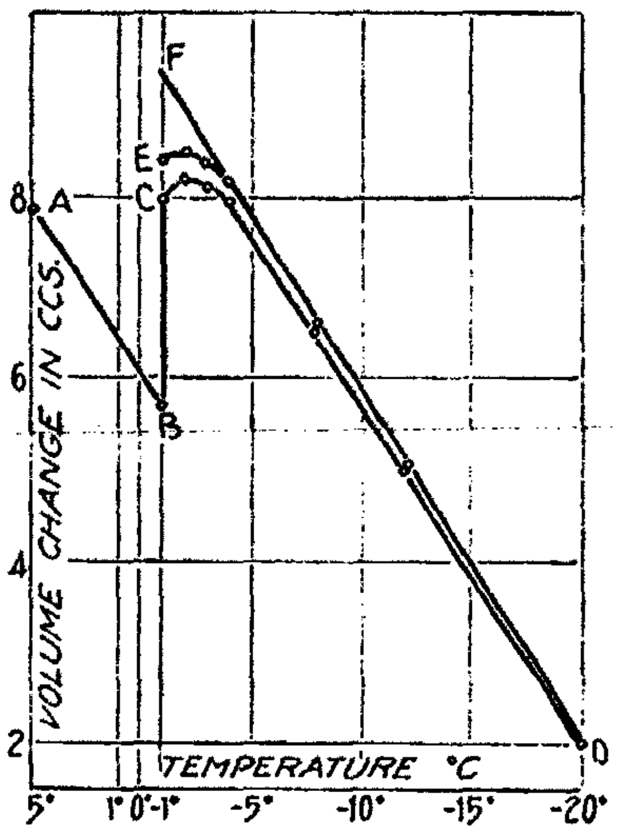

FIG. 2

In such systems as those considered here the 'capillary-adsorbed' water, as it is called by Bouyoucos, is held in two ways: some little of it is held as an adsorbed film round the particles of material, but by far the greater portion is present as annular water wedges between the grains. These two kinds of water, although regarded as one kind by Bouyoucos, Parker and others, exist probably under very different mechanical conditions. The adsorbed film is held on the surface of the particles by cohesive forces of great magnitude and it has been calculated, from certain experimental data, that such films may be under pressures of the order of magnitude of 10000 to 20000 atmospheres with corresponding increase in density.[2] The water wedges however, owing to the concavity of their menisci and when the diameters of the menisci are less than 3μ, are probably under negative pressure or tensions—that increase very rapidly with decreasing diameters.

Thus[3] the tension is connected with vapor pressure by the relationship

$$Q = RT\rho \cdot \log_{10} \frac{p_0}{p_1} - P_0$$

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[1] See ref. 1, p. 362.

[2] A. M. Williams: Proc. Roy. Soc. 98 A, 223 (1920); Harkins and Ewing: J. Am. Chem. Soc. 43, 1787 (1921).

[3] F. J. W. Whipple: Proc. Phys. Soc. Lond. 34, 1 (1922).

in which Q= tension, R = gas constant, T = absolute temperature, p_0 = vapor pressure of water in bulk *i.e.* over a plane surface, p_1 = the vapor pressure of water over the meniscus, P_0 = atmospheric pressure all measured in C. G. S. units, and ρ = density of water. The tube radius, r, can be calculated from the relationship

$$\frac{2\sigma}{r} = g\rho h = RT\,\rho \log_{10} \frac{p_0}{p_1}$$

in which σ = surface tension, whence

$$Q = \frac{2\sigma}{r} - P_0$$

Thus when the diameter of the meniscus has been lowered to 2.4 $\mu\mu$ (corresponding for example in the case of a Rothamsted clay subsoil with 55.4 percent clay fraction, to a water content of 7.5 percent[1] the tension may be as high as 1170 atmospheres. Assuming that the compressibility and extensibility curves for water are continuous[2] and extrapolating to a pressure of −1170 atmospheres the volume of the water would be over 7 percent greater than its volume in bulk.[3] The expansion on freezing according to Foote and Saxton's figures is 9.32 percent, or according to Bunsen's data 9.07 percent. The actual expansion therefore due to the freezing of such water in this particular case would be not 9 percent but 2 percent. Since the amounts of water frozen is calculated from the magnitude of the expansion 78 percent of the water in the example cited would be returned as 'unfree' *i.e.* as unfrozen at 78°C. The validity of the conclusions drawn from dilatometric work depends, as Foote and Saxton themselves point out, on the density of capillary water being the same as that of water in bulk and their work on lampblack certainly appeared to show that this assumption was correct *for lampblack.* It was therefore assumed to hold also for hydrogel. This conclusion however may be questioned. The curve for lampblack[4] (Fig. 3) differed in some important respects from those for hydrogels and soils. Both CD and D'F (Fig. 3) were straight but were not coincident over any part of their course. D'F was practically parallel

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[1] E. A. Fisher: Proc. Roy. Soc. **103** A. 139 (1923).

[2] This was shown to be the case by A. M. Worthington: Phil. Trans. **183** A, 355 (1892) for pressure ranges of −17 and +12 atmospheres for alcohols.

[3] It is not desired to lay any particular stress on these values of 7 percent and 1170 atmospheres. The former is the result of a particularly large extrapolation and the latter rests on the applicability of considerations of surface tension to pores of extremely small dimensions. Both may be unsound in such extreme cases but, as in the application of the gas laws to the concentrated solutions, the orders of magnitude may be right even though the actual values are probably far from correct. In any case the relations between vapor pressures and tensions of capillary columns do not depend on surface tension considerations and are more reliable. The existence of such tensions in capillary liquid columns has been used by Whipple (loc. cit) as an explanation of the action of a hair hygrometer and by the present writer [(J. Agri. Sci. **14** (1924)] to explain residual shrinkage in soils and clays.

[4] J. Am. Chem. Soc. 39, 627 (1917).

to AB as in other cases but no curvature was exhibited by any part of the curve. The divergence of CD and D'F seems to indicate that some capillary water was being frozen along CD: it is certainly difficult to attribute any other significance to this divergence. At the same time it is equally difficult to see why progressive freezing of apparently such considerable quantities of water should not be accompanied by curvature between C and D, especially just below C. Such curvature invariably occurs with soils and hydrogels. It corresponds to the fact that for different decrements of temperature the amount of water freezing per given decrement diminishes at a rapidly increasing rate, and this simply means (a very obvious conclusion in the case of granular media in which the capillaries are in the nature of water wedges) that on any probable distribution of capillaries as regards size a group of large capillaries will contain a larger total amount of water than a group of smaller ones. Thus if there are present a series of pores of circular cross section of radii $r_1 > r_2 > \ldots r_n$, the water in which would freeze at $-t_1°$, $-t°_2, \ldots -t°_n$, and the numbers of each were $n_1, n_2, \ldots n_n$. Then the volume of each group would be $\pi n_1 r^2 l_1$, $\pi n_2 r^2 l_2, \ldots \pi n_n r^2_n l_n$ in which $l_1, l_2, \ldots l_n$ are the lengths of the pores. The freezing curve CD would be straight (assuming constancy of density for the water) only in the very improbable contingency of $\pi n_1 r_1^2 l_1$, being equal to $\pi n_2 r_2^2 l_2$, being equal to $\pi n_n r^2_n l_n$. In all cases (except lampblack), where the curvature below C is slight, CD and DF lie relatively close to each other. Such is the case with alumina for example which has little capillary water but much 'combined' water. Lampblack on the other hand seems to have much capillary water but no 'combined' water. Moreover, in spite of the large amount of capillary water below −6° indicated by the cooling curve, no ice melted on warming to −6° which was the highest temperature of re-warming attained in Foote and Saxton's experiments: the warming curve indicates the absence of capillary water up to −6°. It was unfortunate that re-warming was not continued to 0°. Lampblack certainly appears anomalous in some respects and the argument based on its behavior that the density of water in soils and hydrogels is that of water in bulk is not convincing.

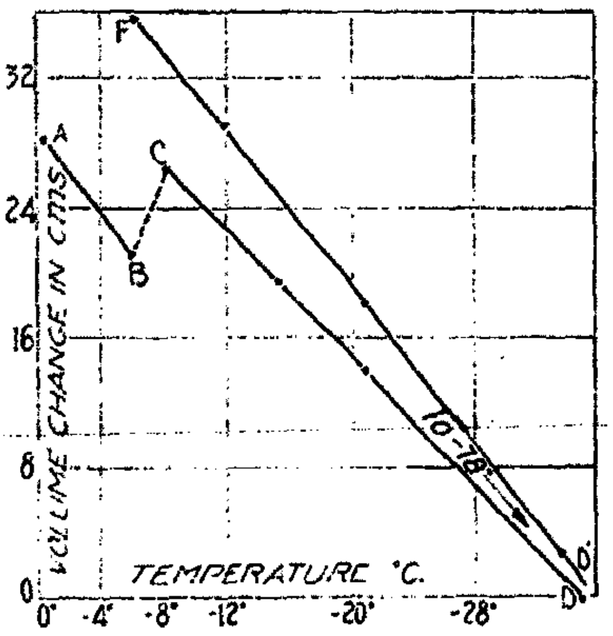

Fig. 3

The above explanation of the so-called 'combined' or unfree water of hydrogels and soils is consistent with many of the experimental data. Thus any process, such as prolonged digestion with water, that would reduce the size of the capillaries would reduce the amounts of both of apparent capillary water (*i.e.* the water that freezes below 0° C) and of 'combined' water (that apparently will not freeze at all). The former would be affected relatively to a much greater extent than the latter because in the latter case although the smaller capillaries would mean less water, the greater tensions due to reduction in size of the smallest capillaries would result in greater extension of the water resulting again in a smaller expansion on freezing. The amount of water returned as combined would be relatively increased thus reducing the absolute amount. Table I, slightly modified from Foote and Saxton's paper, illustrates this.

TABLE I

Apparent Capillary and Apparent Combined Water in Silica Gel

Material	Apparent Cap. Water % of dry Wt. of SiO_2	App. Combined Water % of dry Wt. of SiO_2
Untreated	57	44.3
Digested with water 24 hrs.	44	39.1
Digested with water 7 days	29	29.9

Again the effect of repeated freezing and thawing, on the amounts of capillary and 'combined' water might be expected to differ with different materials as was actually found to be the case by Bouyoucos. With granular material like sands and sandy loams comparatively poor in colloidal matter little effect would be expected. With clay soils rich in colloidal matter repeated freezing would tend to flocculate the colloids, causing some slight approximation to silts:[1] one would expect in this case a reduction in the amount of 'combined' water. With silica gel in which the water is present not as annular water wedges as is the case with silts but in thick-walled actual capillary pores little effect would be expected. These expectations are quite borne out by the data given in Table II. Lampblack again appears to be anomalous.

Such an explanation is also consistent with the fact that the amount of water that apparently fails to freeze is quite independent of the total moisture content. In any given annulus as the temperature is lowered the water would presumably freeze from the surface, *i.e.* the meniscus, inwards. A fresh meniscus, smaller in diameter, would be formed and the unfrozen wedge would be lower in vapour pressure and freezing point and, if the above considerations are valid, under greater tension and therefore of slightly greater relative volume. Provided the lowering of temperature be brought about gradually, as is generally the case, so that equilibrium can be established at each temperature the amount of so-called 'combined' water should obviously be independent of the total moisture content. If the system could be very rapidly cooled to a low temperature, say −78°, so that the mass froze rapidly thereby affording insufficient time for the progressive adjustments in vapour pressure and tension to occur, it is not unlikely that the amount of 'combined' water would be found to be dependent on the total moisture content. This however does not appear to have been investigated.

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[1] Cf. S. U. Pickering: Proc. Roy. Soc. **94** A, 315 (1918).

TABLE II

Effects of Repeated Freezing and Thawing on the Amount of Water that failed to freeze at −78°C (Bouyoucos)

Material	Times frozen	Water that failed to freeze ccs.	Material	Times frozen	Water that failed to freeze ccs.
Quartz sand	1	0.00	Wisconsin superior Clay	1	2.40
	2	0.00			
Fine sandy loam	1	0.80		2	1.80
	2	0.80		3	1.80
	3	0.80	Silica	1	1.60
				2	1.60
Loam	1	1.60			
	2	1.60	Muck	1	1.20
	3	1.60		2	1.00
				3	1.00
Heavy brown silt loam	1	2.40	Peat	1	3.60
	2	1.75		2	2.90
	3	1.75		3	2.90
Heavy dark brown silt loam	1	2.45	Lampblack	1	0.90
	2	1.85		2	0.46
				3	0.10
				4	0.10
Clay	1	2.90			
	2	1.90			
	3	1.90			

Summary

The dilatometric studies of Bouyoucos and his co-workers on soils and of Foote and Saxton on inorganic hydrogels appeared to indicate that much of the water in such systems failed to freeze even at temperatures as low as 78°C and it was concluded that such water cannot be present as free liquid water but must be physically adsorbed or chemically combined or in solid solution. In the above note these conclusions are criticised. It is pointed out that water present in very fine capillary tubes or pores must be under considerable tension and hence possibly the density of such water is not necessarily the same as that of water in bulk. The conclusions of the workers cited rest on the assumption that the density of water in such capillary systems is the same as that of water in bulk. Until this point is cleared up by further experimental work it is difficult to accept these conclusions based as they are solely on dilatometric studies.

The writer is glad to record his indebtedness to Professor J. W. McBain, F.R.S., for helpful criticism in the preparation of this paper.

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THE PHYSICAL CHEMISTRY OF DYEING: SUBSTANTIVE DYES

BY T. R. BRIGGS

The term "substantive" as applied to dyes was introduced originally by Edward Bancroft[1] in the following words. "To me, however, colouring matters seem to fall naturally under two general classes; the first including those matters, which, when placed into a state of solution, may be fixed with all the permanency of which they are susceptible, and made fully to exhibit their colours in or on the dyed substance, without the interposition of any earthy or metallic basis; and the second, comprehending all those matters which are incapable of being so fixed, and made to display their proper colours, without the mediation of some such basis. The colours of the first class I shall denominate *substantive*; using the term in the same sense as it was employed by the great Lord Verulam, as denoting a thing solid by, or depending only upon, itself; and colours of the second class I shall call *adjective*, as implying that their lustre and permanency are acquired by their being adjected upon a suitable basis."

Having thus defined the term and having pointed out that certain coloring matters, adjective to cotton, might be, and actually were, substantive to wool, Bancroft proceeded to describe the substantive colors which were available at that time. His list included Tyrian Purple (the secretion of a certain shellfish), Indigo, Turmeric, Safflower, and the various mineral colors. In regard to the latter colors it is interesting to read[2] that "the affinity between cotton and the oxide of iron is so strong, that by simply moving the former about in water, wherein the sulphate of iron has been dissolved and left exposed to atmospheric air for a few days, it will gradually attract and take to itself every particle of the metallic oxide."

None of the early coal tar colors appears to have been substantive to cotton, and it was not until 1884, when Böttiger discovered Congo Red, that an artificial dye, definitely substantive to cotton, as well as to wool and silk, became available. Since the introduction of Congo Red, many other substantive cotton dyes have been brought into use, notably the Mikado colors and the Primulines. The majority of these dyes are also substantive to wool and silk.

In the modern classification of dyes, adopted by technical colorists, the term "substantive dye" has taken on a rather specialized and narrow meaning. According to Matthews[3] the so-called substantive dyes "include derivatives of benzidine, tolidine, diamidostilbene, and various azoxydiamines; they also include certain derivatives of stilbene, such as the Mikado colors. . . . Another class of direct cotton or substantive dyes is not included in the azo dyes

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[1] "Philosophy of Permanent Colours," 1, 118 (1813).

[2] Bancroft: Ibid., 1, 313 (1813).

[3] "Application of Dyestuffs," 275 (1920).

at all, but is derived from certain bases made from sulphur compounds of paratoluidine or its homologues; these form the primuline group of dyes." The members of this group of dyes, all more or less 'soluble' in water, are similar[1] chemically to the acid dyes, being employed in the dyebath in the form of their sodium salts or as the free dye acid; they differ markedly, however, from the acid dyes in their mode of application to the fiber.[2]

In the broad sense of Bancroft's definition, and because of their marked similarity to the substantive dyes, (as defined by Matthews), in respect of their behavior in the dyebath and toward the fiber, one should include among the substantive dyes the Immedial or Sulphur dyes,[3] the Vat dyes (such as the leuco form of Indigo),[4] suspensions of the inorganic colors,[5] and certain colloidal developing agents, such as those of the Naphthol AS series[6]. Under certain circumstances some of the acid[7] and basic dyes[8] appear to behave like substantive dyes.

Dyeing with Substantive Dyes, Comparison with Acid Dyes

In practice,[9] the substantive dyes are employed in either neutral, acid, or alkaline dyebaths, usually with the addition of an assistant, the action of which is to effect an increase in the amount of color adsorbed by the fiber and to further the exhaustion of the dyebath. These assistants are stated to be salts, such as sodium chloride or sodium sulphate, though as a matter of fact acids and bases act in the same way. Thus we have found that *both* hydrochloric acid and sodium hydroxide, in moderate amounts, cause an increase in the quantity of Buffalo Direct Red adsorbed by cotton, precisely as is done by sodium chloride or by sodium sulphate. Because of the rather striking assisting action of salts, the substantive colors are often spoken of as 'salt' dyes.

The substantive dyes differ distinctly from the acid dyes in the effect produced on the dyeing process by bases and salts containing univalent cations, even though the two classes of dyes are chemically similar. Sodium hydroxide acts normally as a restrainer[10] with acid dyes, but as an assistant with substantive dyes, while hydrochloric acid may act as assistant with both. Sodium chloride is without much effect in the case of acid dyes, but is an active assistant with the substantive class. The difference is marked in the case of sodium

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[1] Cf. Haller: Kolloid-Z., 29, 95 (1921).

[2] Cf. Matthews: "Application of Dyestuffs", 595 (1920).

[3] Cf. Biltz and Behre: Ber., 6 38, 2973 (1905).

[4] Cf. Haller and Nowak: Kolloidchem. Beihefte, 13, 94 (1921).

[5] Biltz: Ber., 37, 1771 (1904); 38, 2963 (1905).

[6] Rath: J. Soc. Dyers and Colourists, 39, 334 (1923).

[7] Cf. Haller: Kolloid-Z., 29, 95 (1921).

[8] Cf. Briggs and Bull: J. Phys. Chem., 26, 873 (1922).

[9] Knecht, Rawson and Loewenthal: "A Manual of Dyeing", 377 (1910); Whittaker: "Dyeing With Coal Tar Dyestuffs," 63 (1919); Matthews: Application of Dyestuffs," 275 (1920).

[10] Cf. Bancroft: J. Phys. Chem., 18, 1, 118 (1914).

sulphate; for the latter is a restrainer[1] with the acid dyes but an assistant with the substantive dyes; this difference has been strongly emphasized by Matthews.[2] I shall therefore take the position that the acid dyes and the substantine dyes do behave very differently, and that the general theory developed by Pelet-Jolivet and by Bancroft for the acid dyes can not be applied, at least without a great deal of straining, to the substantive colors.

While a number of theories have been proposed in explanation of the peculiarities of substantive dyes—notably by Weber, Dreaper, Biltz, Bayliss, and more recently by Haller and by Auerbach—these theories are either incomplete or unsatisfactory and they seem to have made little impression; for Whittaker[3] says that "at the present time it is impossible to offer any definite opinion on the theory of the dyeing of the direct cotton dyestuffs", and Matthews, with a hopelessly vague group of Fourteen Points[4], gets nowhere. It is the purpose of this preliminary paper to show that a satisfactory working theory of substantive dyes can be proposed and that this theory is a modification or an amplification of the earlier theories of the four investigators named first in the preceding sentence.

Some Properties of Aqueous Solutions of the Substantive Dyes

The technical substantive dyes, with which various soluble impurities are invariably found, pass more or less readily into solution in water, more easily when the latter is warm. These solutions are similar in properties to the soap solutions, and, like the latter, they are undoubtedly colloidal,[5] or at least contain ultramicroscopically resolvable 'colloidal ions'. As one might expect, therefore, the strongly flocculated gel, or the dyestuff in the form of crystals, is virtually insoluble in water, as Haller and Nowak have pointed out.[6] The dialyzed solutions, like those of the soaps, are excellent conductors; they exert in a collodion osmometer a surprisingly high apparent osmotic pressure; in the absence of a membrane they possess an easily measurable power of diffusion, though in general they diffuse far less rapidly than the acid and basic dyes; and they invariably contain amicrons or ultramicrons when viewed in the ultramicroscope. It is possible to bring about an increase in the size of the ultramicrons and a corresponding decrease in the degree of dispersion, without causing any visible or actual flocculation of the suspended dye—a property of

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[1] Cf. Briggs and Bull: J. Phys. Chem., 26, 845 (1922).

[2] "Application of Dyestuffs," 595, 596 (1920).

[3] "Dyeing with Coal Tar Dyestuffs," 64, (1919).

[4] "Application of Dyestuffs," 600 (1920); Cf. Ganswindt: "Theorie und Praxis der modernen Färberei," 2, 7, (1903).

[5] Krafft: Ber., 32, 1608 (1899); Raehlmann: Physik Z., 4, 884 (1903); Teague and Buxton: Z. physik. Chem., 60, 469, 489 (1907); 62, 287 (1908); Freundlich and Neumann: Kolloid-Z., 3, 80 (1908); Hober and Chassin: Ibid., 3, 76 (1908); Sheppard: Proc. Roy. Soc., 82 (A), 256 (1909); Biltz and von Vegesack: Z. physik. Chem., 68, 357 (1909); 73, 481 (1910); Vignon: Compt. rend., 150, 923 (1910); Bayliss: Kolloid-Z., 6, 23 (1910); Haller: Färberzeit., 25, 301, 321 (1914); Wo.Ostwald: Kolloidchem., Beihefte, 10, 197 (1919); Haller and Nowak: Ibid., 13, 61 (1921); Haller: Kolloid-Z., 31, 295 (1922); cf. also Knecht and Batey: J. Soc. Chem. Ind., 28, 697 (1909).

[6] Kolloidchem. Beihefte, 13, 86 (1921).

the substantive dye solutions which is of the utmost significance in the theory of substantive dyeing. Increase in size of aggregates is observed as the concentration of the dye is increased, or as the temperature is lowered; at low temperatures concentrated solutions of the substantive dyes set to a jelly. Decreased dispersion is also caused by destabilizing electrolytes, while electrolytes in excess bring about flocculation.[1] The growth of aggregates is opposed by stabilizing protecting colloids, such as gelatin.[2] Practically all of the very complete evidence now available supports the conclusion that in neutral or alkaline dyebaths the substantive dyes are present as electronegative colloids capable of a very high degree of dispersion in the absence of destabilizing agents.

Adsorption of Substantive Dyes from Aqueous Solution

Weber and others[3] have shown that the substantive dyes are taken up by fibers in the form of their undissociated salts and Weber has also remarked that cotton takes up these dyes in exactly the same way that it does tannin in the tannin-mordanting process. Witt[4] therefore assumed that the substantive dyes form solid solutions in the fiber. However, von Georgievics,[5] Biltz,[6] and Schaposchnikoff[7] have obtained typical adsorption isotherms for substantive dyes and cotton, and though, in view of the interesting experiments of Reinders and Lely,[8] this may not be regarded as conclusive evidence of adsorption, the majority of recent investigators are agreed that substantive dyes are adsorbed by the fiber and not dissolved. As to the chemical theory, it should be observed that there is no evidence whatsoever that chemical compounds between these dyes and fiber exist.[9] It will be assumed in what follows that dyeing with substantive dyes is simply a case of adsorbing from suspension a colloid the degree of dispersion and the stability of which are capable of considerable variation.

Distribution of a Colloid between an Interface and the Distribution Medium

The adsorption of a colloid by a solid adsorbent, which for convenience one may consider a fiber to be, can be regarded as a process of distribution of the colloid between the surface of the solid and the bulk of the liquid medium. It will therefore be profitable to consider briefly the general problem presented

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[1] Cf. Biltz and von Vegesack: Z. physik.,Chem. 73, 481 (1910); Wo. Ostwald: loc cit.; Auerbach: Kolloid-Z., 31, 37 (1922).

[2] Cf. Bayliss: Kolloid-Z., 6, 23 (1910): also Biochem. J., 1, 175 (1906).

[3] J. Soc. Chem. Ind., 13, 120 (1894); Gnehm and Kaufler: Z. angew. chem., 15, 345 (1902); Boeseken, Tergau and Binnendijk: Chem. Abstracts, 21, 893 (1919).

[4] Cf. Haller and Nowak: Kolloidchem. Beihefte, 13, 86 (1921).

[5] Zeit. Farben-Ind., 2, 253 (1903).

[6] Ber., 38, 2963 (1905); Cf. Biltz and Steiner: Kolloid-Z., 7, 113 (1919).

[7] Z. physik. Chem., 78, 209 (1911).

[8] Cf. Reinders: Kolloid-Z., 13, 96 (1913); Kruyt and van der Made: Chem. Abstracts, 12, 1701 (1918).

[9] Cf. Bancroft: J. Phys. Chem., 18, 1, 118, 385 (1914); 19, 50, 145 (1915); also King: Brit. Assoc. Report (Colloid Chemistry), I, 20, (1917);

by the distribution of a colloid between an interface and the dispersion medium. The conclusions drawn from such a consideration of the general problem will in turn be made the basis of a theory of dyeing with the colloidal dyes, to which class, as we have seen, the substantive dyes belong.

It has long been recognized that colloids peptized in water, as well as finely divided solids suspended in the same medium, tend to pass into the interface between two phases, one of which is the aqueous dispersion medium and the other is solid, liquid or vapor.[1] Without entering into the causes of this action in each of the three cases, one may look upon the process as an example of adsorption by or at surfaces, and this in turn may be considered to be a species of competition[2] between the two phases—liquid-solid, liquid-liquid, or liquid-vapor—for possession of the finely divided or peptized component. In a previous paper[3] emulsions have been considered from this point of view.

There is therefore good reason to suppose that, since surface and dispersion medium are competing for the suspended material, anything that adds to the stability of the suspension will act against adsorption, while anything that lessens stability will aid adsorption. That is to say: a finely divided solid or colloid in suspension should become decreasingly interfacial[4] in the presence of a peptizing agent, but increasingly interfacial in the presence of a flocculating agent, providing these agents themselves are not strongly interfacial. If an added peptizing agent is strongly interfacial, it may carry with it into the interface the suspended material and thus cause an increase in the apparent adsorption. A possible example of this is the inactivation of hemolytic complement by shaking with air.[5] The serum contains globulin, which is interfacial under the conditions of the experiment and carries the adsorbed enzyme (a colloid) with it.

While a flocculating agent will tend to force the suspended colloid into the interface, it should not be present in amounts large enough to produce actual coagulation. If the latter occurs, the agglomerated flocks may be too large to be retained in the interface and will therefore not be adsorbed, at least strongly. Since flocculating agents in amounts insufficient to produce actual coagulation are known[6] to destabilize sols by decreasing their dispersion, such agents will aid in the adsorption of a colloid up to the point of flocculation but beyond this point will act in the opposite direction. The amount of adsorbed colloid in the interface will therefore pass through a *maximum* as the concentration of the flocculating substance is increased beyond its coagulating value. Such adsorption maxima have been observed,[7] and they show, in

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[1] Cf. Bancroft's summary: J. Phys. Chem., 19, 363, 527 (1915).

[2] Cf. von Hahn: Kolloid-Z., 19, 217 (1921).

[3] Briggs: J. Ind. Eng. Chem., 13, 1908 (1921).

[4] Cf. Bancroft's definition: J. Phys. Chem., 19, 307 (1915).

[5] Schmidt and Liebers: Chem. Abstracts, 8, 371 (1914).

[6] Note Picton and Linder's work on the "degradation" of arsenious sulphide sols by sodium-chloride. J. Chem. Soc., 73, (1895).

[7] Pelet-Jolivet and Siegrist: Kolloid-Z., 5, 235 (1909); Endler: Biochem. Z., 42, 440 (1912); Auerbach: Kolloid-Z., 19, 190 (1921); 30, 166 (1922); cf also Dreaper: "Physics and Chemistry of Dyeing," 261 (1906).

reality, that a dispersed colloid is most strongly adsorbed when its dispersion has some intermediate value, as Wo. Ostwald[1] has suggested.

Flocculating agents are not the only cause of decreased stability and correspondingly increased adsorption within limits, for the stability of a sol may change with the temperature, with age, and with its previous history. The stability and the dispersion decrease with increase in concentration of the sol, which may have something to do with the fact, which has puzzled some of us, that more is adsorbed from a concentrated sol than from a dilute one, and the adsorption curve looks like the typical isotherm obtained with a dissolved adsorbed substance.[2] In this connection it is interesting to note that Metcalf[3] observed semi-solid films on the surface of peptone solutions only when the latter were concentrated. It is possible that in the concentrated sol the peptone became less stable by agglomeration and thus more strongly interfacial in accordance with the theory.

In a previous paper,[4] I have applied the present theory of distribution to emulsions of benzene or kerosene in water. Dialyzed hydrosols of ferric oxide or arsenious sulphide were found to have little emulsifying action because the suspended material was not sufficiently interfacial. On adding a weak flocculating agent such as sodium chloride, however, the sols were destabilized and the colloidal material became sufficiently interfacial to form the films necessary for an emulsion. It was also shown that the suspended material became less interfacial when the destabilization was carried far enough to produce extreme flocculation.[5]

It is known that red hydrosols of gold are more highly dispersed and contain a more effective peptizing agent than is the case with the blue ones.[6] Consequently gold should be more strongly interfacial with blue sols than with red. This is exactly what Reinders[7] found was the case when the sols were shaken with organic liquids such as isobutyl alcohol or ether. He also showed that the addition of a further stabilizing agent, such as gum arabic, to the sol prevented the particles of metal from collecting as a film at the dineric interface.

The importance of the degree of stability of the sol has been brought out and very generally recognized in many cases where the adsorption of a suspended colloid by a solid has been studied. Biltz[8] particularly emphasized it in his work on dyeing with sols of colored inorganic substances. He pointed

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[1] "Grundriss der Kolloidchemie," 417 (1910). Cf. Traube and Shikata: Kolloid-Z., 32, 316 (1923).

[2] Cf. Briggs: J. Phys. Chem., 19, 210 (1915).

[3] Z. physik. Chem., 52, 1 (1905); cf. Bancroft: J. Phys. Chem., 19, 527 (1915).

[4] J. Ind. Eng. Chem., 13, 1008 (1921).

[5] I once tried an experiment on the flotation of arsenious sulphide, in the form of its sol, in a small Janney oil-froth flotation machine. No sulphide was floated until the sol was destabilized by the addition of a little sodium chloride, whereupon the sulphide became interfacial and was carried into the froth.

[6] Zsigmondy: "Kolloidchemie," 99, (1912).

[7] Kolloid-Z., 13, 235 (1913).

[8] Ber., 37, 1766 (1904).

out that weak flocculating agents favored dyeing, while peptizing agents such as soap or gelatine had an opposite effect. His experiments with gold sols are in line with those of Reinders just discussed, for the stable red sols did not dye silk while the less stable bluish ones did so. Abderhalden and Fodor[1] showed that salts which dehydrate proteins (and hence tend to flocculate their sols) favor the adsorption of proteins by animal charcoal, while on the other hand Biltz[2] has found that salts having a peptizing action on albumin cause less of the latter to be adsorbed by hydrous ferric oxide. Palme[3] reported that destabilizing salts favored the adsorption of ferric oxide from its sol by casein and Sanin[4], when mordanting with tannin, found more of the latter on the fiber when sodium chloride was present in the tannin solution.

Substantive Dyeing

I assumed on a previous page that dyeing with the substantive dyes is simply a case of adsorbing from suspension a colloid, the degree of dispersion and the stability of which are capable of considerable variation. Dyeing with these colors becomes, therefore, a very important special instance of the general process of colloid distribution, of which the theory has just been outlined. This theory may now be re-stated in terms of the substantive or colloidal dyes as follows:

A weak flocculating agent added to the dyebath will produce an increase in the amount of dye taken up by the fiber, providing the dye is not actually thrown out of suspension during the process of dyeing. In the latter case, a flocculating agent active enough to produce actual coagulation will cause the fiber to take up less dye. In consequence of these opposed effects, the amount of dye taken up by the fiber will increase to a maximum and will thereafter diminish, as the concentration of the flocculating agent is made greater. It should be observed that the theory has nothing necessarily to do with the question of fastness to light or to washing. Fastness to washing is probably determined largely by subsequent changes which the dye may undergo after it is taken up by the fiber.

A peptizing agent added to the dyebath will cause a decrease in the amount of dye taken up by the fiber, unless the peptizing agent is a second colloid which is itself strongly adsorbed by the fiber. In the latter case since by definition the peptizing colloid adsorbs the dye, it may carry dye with itself on to the fiber, and the latter may take up more dye than it otherwise would. It is possible, though not proved as yet, that this sometimes happens when soap or impure gelatin are used in the dyebath. A second colloid adsorbed by the fiber would act, in other words, as a mordant.

The question of the electric charge on the fiber and on the particles of dye in suspension has been omitted in this discussion. This question has been con-

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[1] Kolloid-Z., **27**, 49 (1920); Fodor: Kolloidchem. Beihefte, **18**, 122 (1923).

[2] Z. Elektrochem., **10**, 937 (1904).

[3] Z. physiol. Chem., **92**, 177 (1914).

[4] Z. Farben-Ind. **9**, 49 (1910).

sidered by Harrison[1] who believes that dye particles or ions may be held on the fiber by electrical attraction when dye and fiber carry opposite charges, but he admits that other causes of attraction must be sought for when dye and fiber carry like charges, as in the case of the substantive dyes on cotton. I have always taken the view[2] that the electric charge of a surface is the *result* of, and not necessarily the *cause* of, adsorption, so in my opinion the charge on fiber and dye is of no prime influence on the process of dyeing with the substantive dyes. Be that as it may, we know that cotton and Congo Red are both charged negatively in weakly alkaline dyebaths and yet the cotton is strongly colored under these conditions.

Applying the principle[3] of the neutralization of adsorbed ions, Bancroft has worked out a modification of the Pelet-Jolivet theory of dyeing and has discussed its bearing on acid and basic dyes, which, except under unusual conditions of the dyebath are *dissolved* in the latter in the form of their simple ions. Bancroft[4] did not consider the substantive dyes, except to suggest that his theory was not based on any hard and fast assumption as to the state of the dyes in solution, but should be equally applicable to the colloidal dyes and to the dyes in true solution. Were this quantitatively the case, sodium sulphate should be a restrainer for substantive dyes, which are chemically similar to acid dyes, whereas it is actually a strong assistant. As a matter of fact, sodium sulphate is an assistant for the substantive dyes because it is a weak flocculating agent and destabilizer, making the dye more interfacial, and thus helping to force it on the fiber. This action of sodium sulphate is far more important than is the restraining effect of the sulphate ion adsorbed by the fiber. It seems probable that a complete theory of substantive dyeing requires that the present theory of distribution and stability should be superimposed on the simpler one applied by Bancroft to the acid and basic dyes. This will certainly have to be done for the acid and basic dyes themselves, for the special case where the dyebath contains a great deal of added electrolyte, because under such circumstances these dyes begin to behave like the substantive dyes and appear to become distinctly colloidal.[5]

In terms of the present theory, an acid, base, or salt which acts as an assistant in the substantive dyebath does so because it makes the particles of dye more strongly interfacial between bath and fiber. This in turn it accomplishes by decreasing the dispersion and stability of the dye in the suspension or sol which constitutes the bath. We have seen that electrolytes are known to produce this effect in the case of various organic and inorganic colloids in suspension, and we should expect the same effect with colloidal dyes. Many instances are indeed known, especially among the experiments of Dreaper and

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[1] Jour. Soc. Dyers and Colourists, 34, 96 (1918); Chem. Abstracts, 13, 265 (1919).

[2] Briggs: J. Phys. Chem., 21, 198 (1917).

[3] Bancroft: J. Phys. Chem. 19, 363 (1915).

[4] J. Phys. Chem., 18, 150 (1914).

[5] Cf. Pelet-Jolivet and Siegrist: Kolloid-Z., 5, 235 (1909); Pelet-Jolivet and Wild: Ibid., 3, 174 (1908), Haller: Ibid., 29, 95 (1921).

his coworkers.[1] Bayliss[2] found that the addition of two percent of sodium chloride to a weak suspension of Congo Red trebled the adsorption of this dye by filter paper. Concerning the effect of this salt, he wrote as follows: "Notwithstanding the fact that no actual precipitation takes place in these experiments, the addition of electrolytes to Congo Red, for example, causes an increase in the size of the colloidal particles, ... so that the solution is on its way to precipitation even when this does not actually occur. The specimen of Congo Red used in all my experiments showed the Tyndall phenomenon very faintly in solution in distilled water; but when sodium chloride was added the beam of light became much more distinct." Bayliss[3] later on brought out the same thing in another way, by determining the apparent osmotic pressure of a solution of Congo Red. He found that the addition of a certain amount of sodium chloride to the carefully purified solution of the dye caused its osmotic pressure to fall from 207 mm to 15 mm in 24 hours, an effect which he ascribed to a decrease in the number, and an increase in the size of the ultramicrons. The agglomerating and destabilizing action of weak flocculating agents in solutions of the substantive dyes may be regarded as absolutely established at the present time.

Weber[4] was among the first to discuss the action of salt assistants in the substantive dyebath. He accounted for this action by assuming that salts decreased the solubility of the dyestuff in the bath. It is worthy of note that Weber pointed out, that of two direct cotton dyes, the one with the lower coefficient of diffusion possessed the greater affinity for the fiber. Since it is now known from the work of Svedberg[5] that the rate of diffusion of a suspended colloid is an inverse function of the size of the particles, Weber's statement is another way of saying that the affinity between dye and fiber becomes greater the smaller the dispersion and the less the stability of the dye in suspension. Weber, however, had rejected a suggestion made by Schultz that the dyes were not actually dissolved in the bath but were in suspension, so he was forced to assume that salt assistants caused a decrease in the solubility of the dye. The same explanation for the action of salts has been used by Dreaper in his "desolution" theory, and by Bayliss in his early work on the adsorption of Congo Red by filter paper, though we have seen that Bayliss probably used the word "solubility" to refer to the degree of dispersion of the dye. Since it has been pointed out previously that Haller and Nowak have shown the substantive dyes to be insoluble in water when crystalline, it is certain that Weber's "decrease in solubility" is equivalent to the decrease in dispersion and stability (destabilization) which we know the dyes undergo when flocculating salts are added to their suspensions.

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[1] Dreaper: "Chemistry and Physics of Dyeing," 251, et seq. (1906).

[2] Biochem. J., 1, 175 (1906).

[3] Kolloid-Z., 6, 23 (1910); cf. Biltz and von Vegesack: Z. physik. Chem., 73, 481 (1910).

[4] J. Soc. Chem. Ind., 13, 120 (1894).

[5] Z. physik. Chem. 67, 105 (1909).

The present theory suggests the possibility of a *decrease* in the amount of substantive dye adsorbed by the fiber when salts are added in quantities sufficient to cause actual flocculation, with precipitation of the dye from the bath. In other words the dye taken up by the fiber should pass through a decided *maximum* as the concentration of the salt is increased, and the position of that maximum, in respect to the concentration of the salt will be determined by the molar coagulating power[1] of the salt. Such maxima will be found in the experiments soon to be described[2]; other instances have been reported by Haller and Nowak and especially by Auerbach.[3] Haller and Nowak infer that such a maximum exists and they account for it essentially in the terms of the present theory when they say:[4] "If the dispersion [of the substantive dyestuff] is too small, precipitation of the dyestuff in the bath takes place, but if it is too large, the dyestuff passes by the surface of the fiber, without being retained by the latter in appreciable amounts" Auerbach, however, accounts for the maximum in dyeing obtained with salts in increasing concentrations by postulating that the salt exerts simultaneously *two* opposite effects, (1) causing a decrease in the amount of dye adsorbed by the fiber by flocculating, at all concentrations, the dyestuff in suspension, and (2) producing an increase in the amount of dye adsorbed by coagulating the dye on the fiber.

Rath[5] has very recently applied what amounts to the present theory to the case of Naphthol AS, which is used in producing developed dyes on cotton. The naphthols of this series are colloidal and they are apparently adsorbed, like the substantive dyes themselves, when cotton is brought in contact with their aqueous solutions. Rath points out that the more dispersed the naphthols, the less is their substantivity. He continues as follows:

"The alkaline solutions of the naphthols of the AS series show at different temperatures the typical behaviour of colloidal solutions; the higher the temperature, the more highly dispersed is the solution and the less is their substantivity. Weaker dyeings are always obtained when impregnating at higher than at lower temperatures, this being especially pronounced with Naphthol AS-SW. Addition of electrolytes (i.e. common salt or Glauber's salt), by lowering the degree of dispersion, causes the dyestuff to go on to the fiber to a larger extent. These additions are, however, dangerous in the case of the naphthols, which do not dissolve easily, such as Naphthol AS-BO or Naphthol AS-SW, because the solution may turn cloudy and soon precipitate. For each of the naphthols there exists a certain optimum in the extent to which it goes on to the fiber. This may be ascertained by impregnating at various temperatures with different additions of electrolytes. If the degree of dispersion of the solution becomes too small owing to too low a temperature when impregnating the cotton, or through too great an addition of electrolytes, then the affinity

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[1] Wo. Ostwald: Kolloidchem. Beihefte, 10, 213 (1919).

[2] These experiments were performed in part by Dr. S. Kakiuchi in this laboratory as long ago as 1917. Publication has been delayed for various reasons.

[3] Kolloid-Z., 29, 190 (1921); 30, 166 (1922); 31, 37 (1922).

[4] Kolloidchem. Beihefte, 13, 89 (1921).

[5] J. Soc. Dyers and Colourists, 39, 334 (1923).

is decreased. The particles, which have thereby become too large, are not able to penetrate through the outside of the fiber. The naphthol in this case is deposited more or less on the outside of the fiber and the fastness to rubbing of the dyeing is poor."

The present theory requires that a peptizing second colloid in the dyebath should bring about a decrease in the amount of dye taken up by the fiber, providing the second colloid does not act as a mordant. Instances of just this effect have been recorded. Bayliss, in the experiments mentioned previously, found less Congo Red adsorbed by filter paper from a bath containing both sodium chloride and gelatin[1] than he did when the bath contained the salt alone. Lichtenstein[2] has reported that "solution salt" (sodium benzylsulphanilate), as well as sodium protalbinate and lysalbinate, causes a decrease in the amount of Indigo adsorbed by cotton; these substances are without doubt peptizing agents toward the colloidal leuco compound in the vat dyebath. Starch has been reported to have a similar effect.[3] On the other hand the addition of tannin to the substantive dyebath, while it might have a stabilizing effect on the dye in suspension, would probably cause more dye to be taken up by cotton, since it is known to be a mordant for the latter material; but so far as I am aware, the experiment has not been tried.

Attention should be called to the fact, in passing, that the theory under discussion obviously is not limited to the relation of colloidal dyes to the ordinary fibers, but can be applied to any case where these dyes are adsorbed, regardless of the adsorbing surface. Thus the general relation found to hold in the case of dye and fiber has been observed to apply to the dye suspensions and oils,[4] and also many inorganic solids.[5]

Experimental Part

The experiments which follow were carried out in this laboratory at various times by Messrs. S. Kakiuchi, M. P. Woodward, D. D. Crandell, F. S. Williamson, and others. Except in the case of Dr. S. Kakiuchi, the work was performed as part of the usual requirement in the course in undergraduate research. The various dyes were made available through the courtesy of the Schoellkopf Aniline and Chemical Works, now part of the National Aniline and Chemical Company, Inc. These dyes included such substantive colors as the following: Buffalo Direct Red, Erie Red 4B, Erie Direct Black GXOO, Erie Direct Green MT, Erie Orange 2R, Niagara Violet 3R, Buffalo Direct Blue G, and Buffalo Direct Yellow CG. The dyes were prepared for use in the experiments by being dissolved in distilled water and the solutions thus obtained were submitted to long continued dialysis until the outer water gave no appreciable

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[1] Cf. also Weyl: Kolloid-Z., **32**, 311 (1923).

[2] Färber-Z., **23**, 205; Cf. Chem. Abstracts, **7**, 2120 (1913).

[3] Tagliani and Krostewitz: Färber-Z., **24**, 143; Chem. Abstracts, **7**, 2310 (1913).

[4] Cf. Sisley: Bull. (4) **21**, 155 (1917).

[5] Cf. Hübner: J. Chem. Soc., **91**, 1068 (1907); Vignon: Compt. rend., **150**, 472; **151**, 72 (1910); Bouchonnet: Orig. Comm. 8th Internat. Cong. Appl. Chem., **2**, 53 (1912); Marc: Z. physik. Chem., **81**, 641 (1913); Feigl: J. Soc. Chem. Ind., **38**, 569A (1919).

test for chlorides or sulphates. Buffalo Direct Red and Eric Red 4B were the only dyes employed to any large extent in the experiments, though it is planned to include a study of some at least of the other dyes in a subsequent report.

Action of Destabilizing Electrolytes

Method 1. The action of destabilizing salts was first studied with Buffalo Direct Red. The latter formed a turbid suspension in cold distilled water, but gave a clear red solution in hot water, which became turbid again when allowed to stand for a long time in the cold. The solution was submitted to dialysis, as noted above, and was adjusted to a concentration of approximately 0.1 percent. On the addition of hydrochloric acid the color of the solution changed to blue, and after a time a blue precipitate made its appearance. The solution was unaffected by the addition of sodium hydroxide in moderate amounts, but became turbid and ultimately was flocculated when such salts as sodium chloride, sodium sulphate, or sodium citrate were added in increasing quantities.

Inch-square pieces of unsized and unmordanted cotton or wool cloth were immersed in the boiling solution of the dye for a period of ten minutes, the volume of the dyebath being maintained more or less constant by adding boiling water from time to time. A single piece of cloth was used in each dyebath, the volume of which was 40 cc. At the conclusion of the dyeing operation the pieces were washed in a very little distilled water and then were dried. The dyeing was done first in a bath containing only the pure dye and then in baths containing known amounts of the different salts.

It was assumed in this experiment that the amount of dye adsorbed by the cloth could be ascertained, at least qualitatively, from the depth of color of the dyed pieces. Accordingly the latter were compared with an arbitrary scale, which was prepared by dyeing inch-square pieces of cotton in the manner described above in baths containing known amounts of pure dye. Number 10 in this scale was obtained by dyeing the piece of cotton in a 0.1 percent solution of the dye; each whole number in the scale represents the color taken up in a dyebath the concentration of which was about *half* of that of the whole number next higher in the scale. Thus the higher the scale number, the deeper was the shade of red on the cotton. In this manner the data of Table I were obtained.

TABLE I

Influence of Certain Salts on dyeing with Buffalo Direct Red

Mols Salt per Liter	Depth of Color (Arbitrary Scale)		
	Sodium Chloride	Sodium Sulphate	Sodium Citrate
0	10	10	10
1/32	10.5	12	12
1/16	11	13.5	14
1/8	12	14	15
1/4	13	15	14.5
1/2	13.5	15	13
1/1	12	14	—
2/1	9	9	—

In the case of each of the salts their addition to the dyebath promotes at first the taking up of dye by cotton, but as their concentration becomes fairly large the opposite effect is observed. The amount of dye adsorbed passes through a maximum, exactly as it should do in view of the theory outlined in the first part of this communication, providing these salts act as destabilizing agents toward the dye suspension. There is no doubt whatsoever that destabilization does occur because in the baths containing salt in twice molar concentration visible flocculation was observed even in the boiling solution and there was evident a distinct turbidity in the baths at the point of maximum dyeing. It is also interesting to note that the point of maximum dyeing occurs at approximately the same *equivalent* concentration with each of the three salts, indicating that their equivalent flocculating power under the conditions of the experiment has about the same value for each.

Similar results were obtained with Erie Red 4B and sodium chloride, sulphate and phosphate; also with sodium chloride and Erie Direct Green M T, Niagara Violet 3R, and Buffalo Direct Blue G. In every instance a decided point of maximum dyeing occurred when the concentration of the added salt was 1/2 or 1/4 Normal.

Method 2.

Since the intensity and depth of color of a dyed piece of cotton may not be a trustworthy measure of the amount of dye adsorbed, the correctness of the results of the previous experiment was checked in a different way. A certain volume of dye solution was heated to boiling and inch-square pieces of cotton were added until the dyebath was practically decolorized. When the dyebath contained no salt 12 pieces were needed to remove the color. When the bath contained sodium chloride, sodium sulphate, or sodium citrate (1/4 mol per liter), 3, 2, and 2 pieces were required respectively. In a similar experiment with Erie Red 17 pieces of cotton were needed to exhaust the dyebath in the absence of sodium chloride, while only 7 were necessary when the bath contained sodium chloride of a concentration equal to that of the point of maximum dyeing. A more complete experiment was then carried out with a 0.025 percent solution of Erie Red, the results of which are given in the next table.

TABLE II

Cotton required to decolorize Dyebath (50cc)

Sodium Chloride Mols per Liter	Cotton required Square Inches
None	76
1/4	28
2/1	74

The numbers of Table II confirm the results obtained by Method 1, since the number of inch square pieces of cotton required to decolorize or exhaust the dyebath passes through a *minimum* as the concentration of salt in the bath is made larger.

Method 3.

The effect of sodium chloride on dyeing cotton with Erie Red was next determined quantitatively by ascertaining the amount of dye actually adsorbed from dyebaths containing different quantities of the salt. This was done by determining the dye content of the bath before and after dyeing, by the use of a titanous chloride solution previously standardized against solutions containing a known amount of dye, essentially as described by Briggs and Bull[1]. The results, which appear in Table III, fully confirm those obtained by the simpler but less exact methods of the previous experiments. As before, maximum dyeing occurs when the sodium chloride content of the bath is 1/4 mol per liter.

TABLE III

Adsorption of Erie Red 4B by Cotton in the Presence of Sodium Chloride

(Each dyebath originally contained 75 milligrams dye in 250 cc; cotton one gram)

Sodium Chloride Mols per Liter	Dye adsorbed per Gram Milligrams
None	24.5
1/8	32.5
1/4	36.5
1/2	33.0
1/1	29.1
2/1	28.0

The three experiments that have been described bring out clearly the fact that below a more or less well defined concentration sodium chloride causes the substantive dyes to become increasingly interfacial and to be adsorbed in larger amount by cotton under the conditions of dyeing employed. It was thought worth while to try a similar experiment, replacing the cotton with a *liquid* practically immiscible with water and incapable of dissolving the dye. Benzene was found to meet these requirements. Equal parts of benzene and 0.1 percent solutions of Erie Red containing known amounts of sodium chloride were shaken in glass-stoppered bottles, and the emulsion of benzene in water formed in each case was allowed to stand undisturbed until the drops of emulsified benzene had risen to the top and had formed a compact layer above the excess of the aqueous dispersion medium. The color of the upper emulsion layer and of the lower aqueous layer was then recorded. The observations appear in Table IV.

Distribution of Erie Red 4B between Water and Benzene

Sodium Chloride Mols per Liter	Color of upper Layer Emulsified Benzene	Color of Lower Layer Aqueous Solution
None	Light red	Deep red
1/16	Light red	Red
1/8	Red	Light Red
1/4	Deep red	Very light red
1/2	Very deep red	Almost colorless

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[1] J. Phys. Chem., 26, 845 (1922).

These observations bring out clearly the action of sodium chloride in favoring the concentration of dye at the benzene-water interface. It is also interesting to note that the dye is an excellent emulsifying agent, as indeed it should be, since it exists in the aqueous phase in the form of a colloid in suspension, and it is not only strongly interfacial even in the absence of destabilizing salt but it is evidently capable of forming a suitably elastic film around the globules of benzene. When no salt was present with the dye relatively little of the latter was carried into the interface and hence little appeared in the emulsion layer and the color of this layer was relatively light. When much salt was added to the aqueous phase containing the dye, the suspension of the latter was destabilized to such an extent as to cause the dye to pass wholly into the emulsion layer, the aqueous layer being rendered colorless and free from dye in any form. In this experiment no point was observed where the dye in the emulsion layer passed beyond a maximum, such as was noted with cotton, because even coarse, flocculent masses of dye, formed in the presence of large amounts of salt, were able to remain, more or less trapped, in the upper layer of emulsion. It is evident from the results of this experiment that the action of salts in the dyebath is not dependent upon the presence, in the bath, of cotton or any solid adsorbent, since essentially the same action takes place when the adsorbent is a liquid, such as benzene.

In order that direct evidence might be obtained to support the contention that salts such as sodium chloride cause a decrease in the degree of dispersion of the dye and a corresponding decrease in stability of the suspension of the dye, the following experiment was carried out. To equal volumes of 0.1 percent solution of Eric Red contained in tubes, known amounts of sodium chloride were added and the mixtures heated to boiling. The appearance of each solution was then recorded. The tubes were set aside to cool and the appearance of the solution in each was noted after 15 minutes and then after 12 hours. When 36 hours had elapsed a fine platinum wire was immersed in the solutions which contained little salt and the depth at which the wire just remained visible was ascertained. The results are assembled in Table V.

TABLE V

Effect of Sodium Chloride on Solutions of Eric Red 4B

Sodium Chloride Mols per Liter	Appearance of the Dye Solution On Boiling	After 15 min.	After 12 hrs.	Depth at which Wire remained visible
None	Clear	Clear	Clear	5.8 cm
1/16	Clear	Clear	Clear	2.8 cm
1/8	Clear	Faintly turbid	Turbid	
1/4	Clear	Turbid	Very turbid	
1/2	Faintly turbid	Flocculated	Flocculated	
1/1	Turbid	Flocculated	Flocculated	

It is certain from these results that sodium chloride does actually cause a decrease in dispersion and in stability. Even when the concentration of salt was only 1/16 molar a faint turbidity was noticeable after 36 hours, for the wire became invisible when immersed to a depth of only 2.8 cm as compared with 5.8 cm with the pure dye. These results were then checked by measuring roughly the power of diffusion of the dye with and without sodium chloride.

A number of test tubes were fitted with one-hole rubber stoppers carrying short diffusion tubes open at the lower end and sealed at the upper end. These tubes were 10cm long and about 2mm in internal diameter; each was filled with distilled water or salt solution, as the case might be. Dye solutions (0.1 percent) were prepared containing known amounts of sodium chloride and portions of these were placed in the test tubes, into which were fitted the diffusion tubes in such wise as to bring the lower open end of the latter 3 mm below the surface of the dye solution. The test tubes were then placed upright in a rack in a constant temperature room and were left undisturbed for a period of five weeks, when the height to which the dye had risen in each diffusion tube was noted. The data follow.

Table VI

Effect of Sodium Chloride on the Diffusion of Some Substantive Dyes

Sodium Chloride	Rise of Dye in Centimeters		
Mols per Liter	Erie Red 4B	Niagara Violet 3R	Erie Black GX OO
None	4.0	3.0	5.0
1/100	3.7	2.7	4.5
1/50	3.5	2.5	4.0
1/10	2.5	2.0	3.0
1/5	1.5	1.0	2.0
1/2	0.0 ppt	0.0 ppt	0.0 ppt
1/1	0.0 ppt	0.0 ppt	0.0 ppt

It has been pointed out that the diffusive power of a colloidal dye, although small, is measurable and is a direct function of the degree of dispersion of the dye in suspension. These data on diffusion, therefore furnish additional proof of the degrading and destablizing influence of sodium chloride on suspensions of typical substantive dyes.

Salts the cations of which are polyvalent, as for example barium chloride or aluminum chloride, are extremely active in flocculating dyes such as Erie Red and the others under investigation. Aluminum chloride is more active than barium chloride, which in turn is far more active than sodium chloride. In view of the present theory, one would expect to find the first two salts acting as dyeing assistants at very much smaller concentrations than are required with sodium chloride. The point of maximum dyeing should also occur at a lower concentration. This is precisely what happens, though the increase in amount of dye adsorbed at the point of maximum dyeing is by no means so pronounced as it is in the case of the sodium salts.[1]

By the use of the procedure denoted as Method 1, a slight but distinct point of maximum dyeing occurred with Erie Red when the dyebath contained 1/8000 mol per liter of barium chloride, or about 1/30,000 mol per liter of aluminum chloride. At greater concentrations, these salts caused the dye

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[1] Cf. Auerbach: Kolloid-Z., 30, 166 (1922).

suspension to become flocculated, and the amount of color taken up by the cotton rapidly became smaller. A second experiment based on Method 2 was also tried. Twelve inch-square pieces of cotton cloth were found necessary to decolorize completely 50 cc of 0.05 percent Buffalo Direct Red solution in the absence of salt, the dyeing being carried out at boiling temperature for 30 minutes. It was then ascertained how much of the different salts was necessary in order that the dyebath might be exhausted under otherwise identical conditions by means of six pieces of cotton instead of the twelve required in the blank experiment. 0.12 mol per liter was required with sodium chloride, 0.001 mol with barium chloride, and only a trace—about 0.00025 mol with aluminum chloride.

Experiments were next carried out with dyebaths of Erie Red containing sodium hydroxide in different amounts. The addition of base was found to produce about the same effect as was caused by sodium chloride, that is, the base acted as an assistant. A point of maximum dyeing was observed when the concentration of base was about 1/4 molar. Beyond this point less color was taken up by the cotton and the dye suspension was visibly flocculated. The same results were obtained with Erie Direct Black. It was also shown, by means of diffusion experiments like those previously described, that addition of sodium hydroxide to the dye cut down the speed of diffusion.

Action of Stabilizing Colloids

It has thus been shown conclusively that destabilizing electrolytes act as assistants toward the colloidal dyes, providing the destabilizing action is not too great. It has been pointed out in the discussion of the theory that a stabilizing agent should have the opposite action in the dyebath and should serve as a restrainer, that is, if it is not itself strongly adsorbed by the fiber. If the last should occur, the fiber would virtually be mordanted and might easily take up a larger quantity of dye.

In testing this deduction, one would naturally turn to some protecting colloid to play the part of stabilizing agent in the dye suspension. Gelatin was thus chosen, but since this substance is known ordinarily to contain small amounts of calcium salts which would have a very powerful assisting action in the dyebath, it was purified carefully by the method recommended by Loeb.[1] Solutions of Erie Red, Buffalo Direct Blue, Erie Direct Green, Niagara Violet, and Erie Direct Black were prepared and cotton was dyed in each of these by proceeding in accordance with Method 1. It was found that when the baths contained 0.5 percent of gelatin, the cotton was colored a decidedly lighter shade as compared with the dyeings obtained in the baths with no gelatin. Dialyzed egg albumin had the same effect qualitatively as gelatin, though in this case dyeing was carried out at room temperature.

It was also found that the restraining action of gelatin became more pronounced as its concentration in the dyebath was increased. While cotton was dyed a dark, somewhat uneven blue in a gelatin-free solution of Buffalo Direct

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[1] "Proteins and the Theory of Colloidal Behavior," 35 (1922).

Blue, the color of the dyed pieces became progressively much lighter as the gelatin content was carried up to 12 grams per liter.

When both gelatin and sodium chloride were present in the dyebath, the assisting action of the salt was more or less neutralized by the restraining effect of the gelatin, as was expected. In terms of the present theory, the position of the point of maximum dyeing got with sodium chloride should be shifted by the addition of gelatin. Since more salt will be required, when gelatin is present, in order that the dye suspension may actually be flocculated, the point of maximum dyeing will occur at higher concentrations of salt when the stabilizing colloid is added to the bath. This conclusion was submitted to test. Erie Red was used, first with no gelatin, and then with one percent of the latter material. The colors of the dyed pieces were compared in terms of the arbitary scale previously used.

TABLE VII

Combined Effect of Sodium Chloride and Gelatin on dyeing with Erie Red 4B

Sodium Chloride Mols per Liter	Depth of Color (Arbitrary Scale) No Gelatin	1 percent Gelatin
None	12	10
1/32	12.5	10.5
1/16	13	10.5
1/8	14	11
1/4	15	12
1/2	14	13
1/1	12.5	13
2/1	0	11
4/1	7	7

The numbers of Table VII show that the expectation of the previous paragraph was realized by experiment. In the absence of gelatin, the point of maximum dyeing occurred in the bath containing 1/4 mol sodium chloride per liter. When gelatin was added, the point was shifted and occurred somewhere between the half molar and the one molar solutions. Besides this, the gelatin had the effect of causing less color to be adsorbed at the maximum, but more color for some distance beyond this point.

The action of gelatin as restrainer was also brought out very strikingly by experiments in which the procedure of Method 2 was used. Erie Red (0.05 percent) was again employed and the least number of inch-square pieces of cotton needed to exhaust the dyebath was determined. The results follow.

TABLE VIII

Influence of Gelatin on dyeing with Erie Red 4B

	Composition of Dyebath	Pieces to Decolorize Dyebath
1	25cc Dye plus 25 cc Water	17
2	Same plus 25 cc 2.5 percent Gelatin	40
3	Same plus 25 cc M/2 Sodium Chloride	7
4	Same plus 25 cc M/2 Sodium Chloride containing 2.5 percent Gelatin	20

It was thought that sodium oleate might have the same effect as gelatin, but this was found not to be the case. Addition of sodium oleate up to one percent in dyebaths containing 0.1 percent of Erie Red caused a progressive increase in the amount of color shown by dyed cotton, though the actual amount of this increase was not very large. The color was brighter and more evenly distributed. It seems probable that something in the soap solution is adsorbed by the fiber and acts as a mordant for the dye, but this is only a guess at present.

Conclusions and Summary

The experiments reported in the preceding pages, while admittedly of a somewhat preliminary nature, appear to be in complete agreement with the general theory of substantive dyes as stated in detail in the introduction to this paper. It is gratifying to note that the results, derived independently and in some cases as early as the summer of 1917, confirm and amplify those of Auerbach previously mentioned. An effort has been made in this paper, however, to show that the phenomena met with in dyeing with *predominantly*[1] colloidal dyes may be explained with the aid of what is known about the distribution of colloids in suspension between an interface and the suspending medium.

The results of this paper may be summarized as follows:

1. The evidence collected by previous investigators shows conclusively that the process of dyeing with substantive or colloidal dyes is simply a case of adsorbing a colloid from its suspension, in which the dispersion and stability are capable of being greatly varied.
2. The adsorption of a colloid from suspension has been considered as a process of distribution between an interface and the suspending medium. Factors which affect this process have been considered.
3. From a consideration of the general process of colloid distribution, a special theory of substantive dyeing has been formulated and tested by experiment.
4. A substance which destabilizes the suspension of the dye will act as an assistant in the dyebath up to the point of actual flocculation.
5. A substance which stabilizes the suspension of the dye will act as a restrainer, providing it does not act as a mordant toward fiber and dye.
6. A stabilizing substance and a destabilizing substance may each exert their specific effects in the same dyebath.
7. Transition dyes undoubtedly exist which combine with their properties of acid or basic dyes the characteristics of substantive dyes.
8. The experiments are being continued.

Cornell University.

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[1] A substantive dye of the sodium salt type which is wholly colloidal in water will behave in accordance with the theory outlined in this paper. If, however, the dye is a semi-colloid (partly in true solution) it will behave partly as an acid dye and partly as a colloidal dye, one or the other behavior possibly predominating. Such a dye might be called a transition dye, and it is very probable, so I am told by Dr. A. W. Bull, that Niagara Violet is an example. Likewise, a semi-colloidal basic dye will behave partly as a basic dye and partly as a colloidal dye, as Briggs and Bull have noted in the case of Methylene Blue.

THE MECHANICAL CONDITION OF COAGULA AND ITS BEARING ON THE THEORY OF COMPLETE COAGULATION. I

BY SHANTI SWARUP BHATNAGAR, KRISHNA KUMAR MATHUR AND
DASHARATH LAL SHRIVASTAVA

Much valuable information regarding the mechanism of the coagulation of colloids has been obtained by a rigorous chemical examination of the precipitates formed as a result of the action of electrolytes on colloidal solutions. In fact the experiments of Linder and Picton[1] and Whitney and Ober[2] on the complete chemical analysis of the precipitates form the pillars on which the theory of coagulation by adsorption has been raised by H. Freundlich.

A thorough and accurate examination of the physical and mechanical condition of coagula ought to be of considerable importance in elucidating the properties and behaviour of colloidal solutions from which the coagula have been formed. It can be seen a priori, for example, that the coagulum of "primary particles" of a colloidal solution would have smaller aggregates if the original sol consisted of smaller particles and of larger aggregates if it was composed of larger particles. Thus it would be possible to get roughly at the average original sizes of various colloidal solutions from the sizes of aggregates in the coagula which preserve their identity and which are similarly obtained by the action of an electrolyte. For even a rough comparison of the sizes of colloidal solutions very complicated apparatus and mathematics have to be used. It is probably on account of these difficulties that the effect of the sizes of particles has not been taken into consideration in any of the well-known theories of coagulation, although such an effect can be easily shown to be important in the following manner:—

Let E be the electrical charge on the ions required to produce "the sign of turbidity" which indicates coagulation of a sol containing particles of equal sizes of radius r

$$\text{Then } Q = V \frac{r^2}{d} k$$

where V is the potential difference, k the dielectric constant of water and d the thickness of the electrical "double layer" and Q the quantity of charge on each particle.

If we assume that the theory of electrical neutralisation of particles represents the process of coagulation faithfully then we have

$$E = nQ$$

where n is the number of particles coagulated by the ions. Keeping the con-

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[1] J. Chem. Soc. 61, 114 (1892).

[2] Z. physik. Chem. 39, 630 (1902).

centration of the dispersed phase as before let us assume that the size of individual particles is reduced to a smaller radius r_1^3

$$\text{then also } Q_1 = V\ \frac{r_1^2}{d}k$$

The number of particles is now evidently increased in the ratio $r^3 : r_1^3$

The amount of electrical charge required to neutralise all the particles in the second sol is

$$E_1 = n\ \frac{r^3}{r_1^3}Q_1$$

$$= n\ \frac{r^3}{r_1^3}V\frac{r_1^2}{d}k$$

$$= n\ \frac{r^3}{r_1}.\ \frac{V}{d}k$$

$$= n.\frac{r}{r_1}\ Q$$

$$= \ \frac{r}{r_1}E$$

$$\therefore \frac{E_1}{E} = \frac{r}{r_1}$$

i.e. the amount of electrolyte required to coagulate a given concentration of a sol would increase with the decreasing size of the particles.

Experimental evidence of Sven Oden on sulphur sol is in agreement with the theoretical conclusions deduced above. Sven Oden[1] investigated the effect of the degree of dispersity of the sol on the coagulation of sulphur suspensions and came to the conclusion that the electrolyte concentration necessary for coagulation increased with decreasing size of particles.

If the theory of coagulation based on the mere preferential adsorption of ions without any reference whatsoever to the electrical nature of the adsorbent ions, be adopted as our guide to the process of coagulation, one would not expect any relationship between the valency of the precipitating ions and the structure of the precipitate. On the other hand if the adsorption of ions by the particles is an electrical process, the structure of the coagulum would indicate to some extent the nature of steps in which combination took place to yield the particular precipitate. The structure of the coagula would probably show some relationship with the valency of the precipitating ion and the degree of dispersity of the sol.

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[1] Cf. Hatschek: "Introduction to the Physics and Chemistry of Colloids", p. 58, 4th edition.

Further, the fact that the coagulation[1] "at any stage" is quantitatively reproducible, postulates that a particular combination of particles (which represents the particular stage) will always be formed provided the conditions of the experimentation remain unaltered.

Thus the prospects of obtaining valuable information regarding the mechanism of coagulation by studying the coagulum at any particular stage of coagulation seem to be very promising. It is in order to get evidence from this new direction, namely, from the structure of the coagula, for or against the present theories of coagulation and to find any relationship if it exists between the valency of the precipitating ions, the original sizes of the colloidal solutions and the particles present in the coagula that the present investigation was primarily undertaken.

Experimental

Stokes' Law for the fall of particles in a viscous medium can be applied to the sizing of particles of coagula. According to this law

$$V = \frac{2}{9} g \frac{\rho - \rho_1}{\eta} r^2$$

where V = constant velocity of the particles
ρ and ρ_1 the specific gravities of the particles and the liquid respectively.
η = viscosity of the latter,
and g = gravity constant.

The above law has been applied by the geologists for the separation of sand, mud and silt in the mechanical analysis of the soil and various forms of elutriators for work have been devised by Schoene, Stadler, Cook and others. Sven Oden[2] has developed a method of calculating the distribution of sizes from "the accumulation curve" obtained by plotting time against the weight of accumulated material on a pan suspended at the bottom of a cylinder containing a suspension of clay. This fascinating method was first employed to obtain information regarding the mechanical condition of coagula of arsenious sulphide, antimony sulphide, manganese dioxide and copper ferrocyanide.

The sol of arsenious sulphide was prepared in the manner advocated by Linder and Picton by dissolving Kahlbaum's pure arsenious oxide in about 12 litres of twice distilled water and passing pure sulphuretted hydrogen in the cold solution. The excess of sulphuretted hydrogen was removed by bubbling hydrogen in large quantities for several days. The absence of the uncombined gas was tested for by the lead acetate reaction. The solution was filtered before use and was stocked in two large hard glass bottles which were kept in a dark room.

Similar precautions were taken in the preparation of large quantities of colloidal solutions of antimony sulphide and Merck's pure potassium antimony tartarate was used in the preparation.

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[1] Cf. Smoluchowski: Z. physik. Chem. 92, 192 (1917); Willows: "General Discussion on Colloids," Trans. Faraday, Soc. and Phys. Soc. Oct. (1920).

[2] Trans. Faraday Soc. 17, Part II (1922).

The colloidal solution of copper ferrocyanide was prepared according to the method described in Zsigmondy's book on colloidal chemistry and Merck's pure reagents were used throughout. The preparations of colloidal solution of manganese dioxide presented some difficulty. The precipitation method of getting the sol proved quite useless. The sol was never stable for more than an hour and fractional coagulation set in automatically during the process of dialysis as well as in the stock bottles.

The method of producing colloidal solution by the reduction of potassium permanganate by manganous sulphate according to the equation

$$2\,KMnO_4 + 3MnSO_4 + 7H_2O = 2KHSO_4 + 5\,MnO_2 + H_2SO_4 + 5H_2O$$

is also useless for our purpose; the sol so obtained being unstable unless some protective colloid like gelatine is added to it. The addition of a substance like gelatine complicates the process of coagulation and interferes with the purity of the sol.

The following method was finally adopted for preparing a colloidal solution of manganese dioxide. N/20 solution of Merck's pure potassium permanganate was prepared and boiled vigorously. Fairly concentrated solution of ammonia was gradually added to the boiling solution and a small portion of the solution was taken out and coagulated with sodium chloride from time to time until it showed complete absence of potassium permanganate. This could be determined very accurately by noting the absence of colour in the supernatant liquid after the coagulum had settled down. The colloidal solution thus obtained could be preserved for months in hard glass bottles well protected against the entry of dust by suitable stoppers.

500 c.c. of colloidal solution were as a rule coagulated by a known amount of an electrolyte. The two were thoroughly mixed by a clean glass stirrer. The coagulum was next transferred to the cylinder for noting the sedimentation equilibrium according to the method of Sven Oden.

Although all the precautions necessary for the constancy of conditions were observed, the results obtained for a particular coagulum were never concordant even when the number of trials made was very large. As a great deal of time was spent in repeating the experiments it would be of interest to show the best results obtained by this method and they are given in Tables I and II.

TABLE I

Coagulum of Manganese Dioxide obtained by coagulating 500 c.c. of Manganese Dioxide sol with 50 c.c. of M/10 solution of Barium Chloride.

Weight.	Time for Trial I.		Time for Trial II.		Time for Trial III.	
	Min.	Sec.	Min.	Sec.	Min.	Sec.
.05 gm.	3	20	3	5	2	45
.10 gm.	5	30	4	50	4	50
.15 gm.	11	55	8	5	10	45
.18 gm.	47	0	24	0	17	10

TABLE II

Coagulum of Antimony Sulphide obtained by coagulating 500 c.c. of Antimony Sulphide sol with 50 c.c. M/10 Barium Chloride.

Weight.	Time for Trial I		Time for Trial II.	
.05 gm.	5 Min.	0 Sec.	8 Min.	0 Sec.
.10 "	10 "	20 "	14 "	40 "
.12 "	16 "	10 "	24 "	35 "
.14 "	39 "	45 "	33 "	45 "
.15 "	53 "	30 "	45 "	40 "

It is evident from the results that the time required to accumulate a given quantity of the coagulum on the pan is not the same in all experiments which should be the case if Sven Oden's method was applicable to these coagula. There is probably a slight tendency in the coagula to form a net-like structure if allowed to stay at rest for a long time and this is likely to interfere with the reproducibility of results by Sven Oden's method.

Reproducible results could, however, be obtained by adopting an elutriator which one of us (K.K.M.) had used at the Royal School of Mines, London. A complete drawing of the elutriator used is given in Figure 1. The elutriating vessel E was set in position according to the special requirement of the experiment as shown in the figure. It was attached to the piezometer tube P, by a long rubber tube to the sliding cistern C. The water was kept at a particular level-head in this vessel by adjusting the entry of distilled water from a large reservoir R so that the water just oozed out into the overflow vessel O through a glass tube. The arrangement for pumping distilled water to the reservoir R are self-explanatory in the figure. The pumps served a double purpose viz., that of pumping water and of filtering the particles as they came out through the nozzle. Precautions were taken to see that the distance between the nozzle and the piezometer scale remained constant during experimentation. The nozzles were standardized

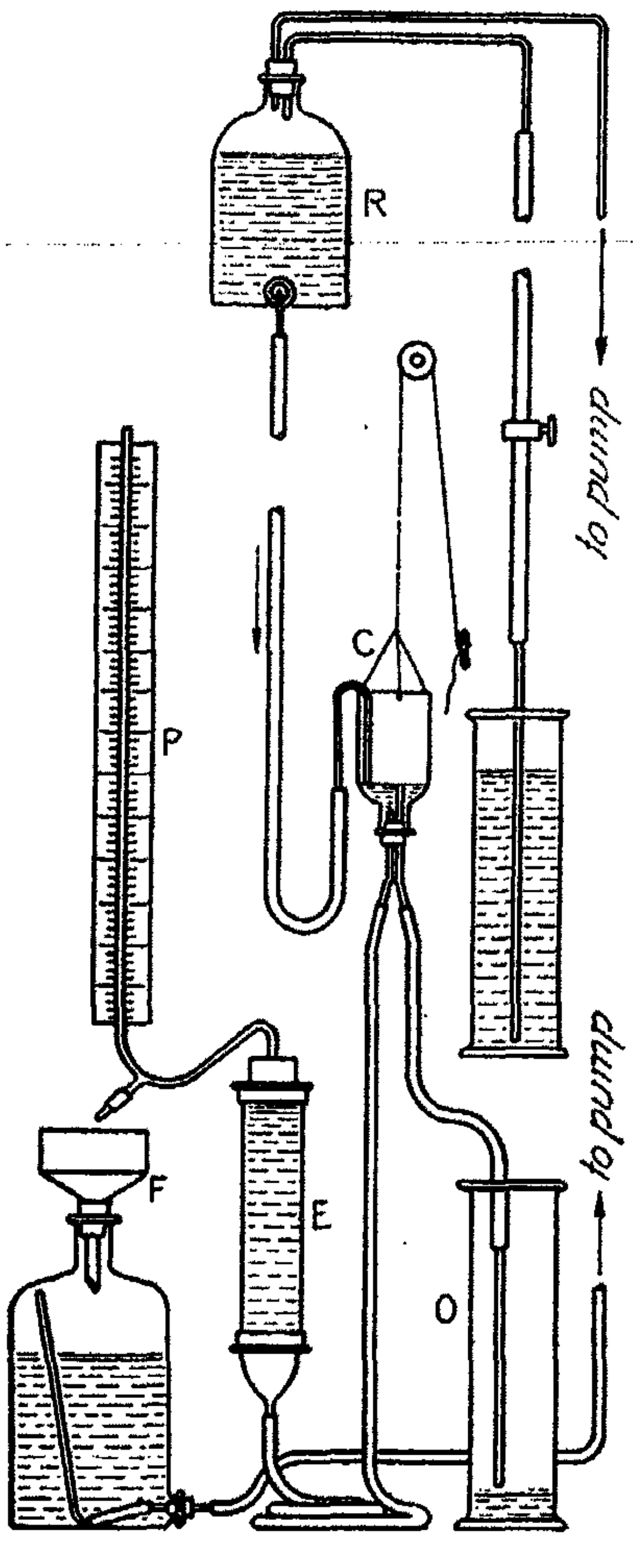

FIG. I

by placing the elutriator in position as shown in the diagram and weighing the quantity of water that flowed out in a minute at various heads through the nozzle. Three nozzles were tried.

The area of the cross-section of the elutriating vessel was next determined at various positions and the mean was found to be 9.6 sq. cm. The velocity cms./min. was calculated by dividing the amounts of water obtained at various heads by the area of the cross section. The velocity head curves are shown in Figure 2. From the curve it is possible to read out accurately the velocity at any position for any nozzle.

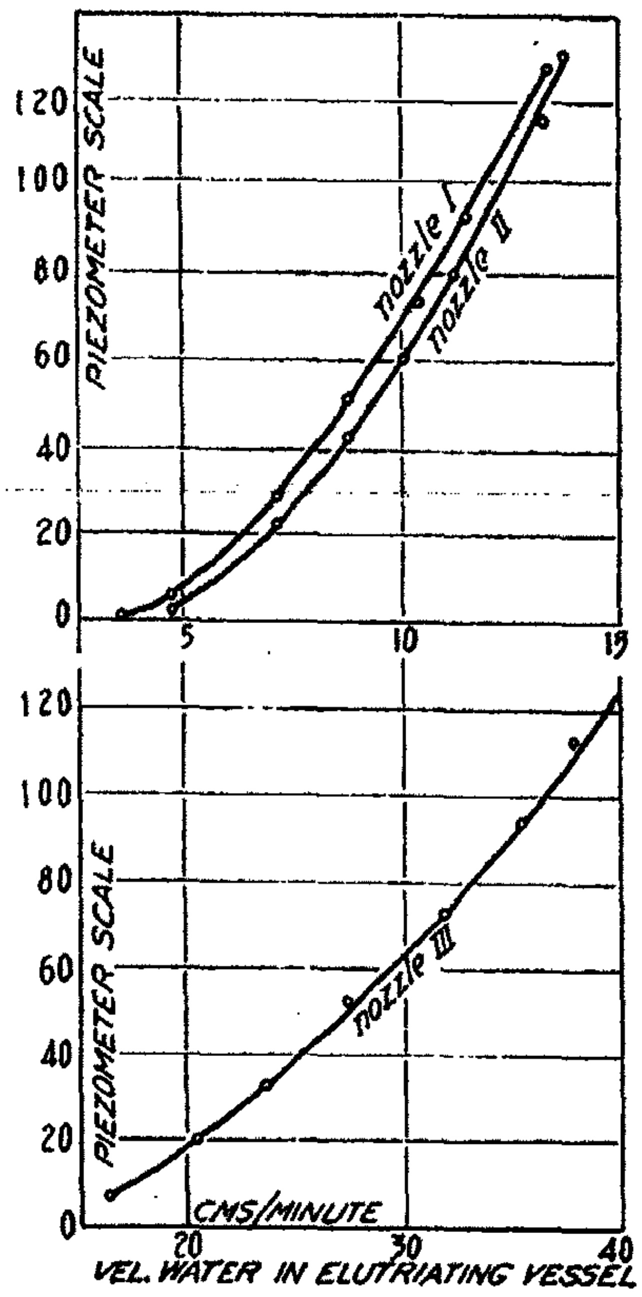

FIG. II

Hydrosols of Antimony and Arsenic Sulphides

500 c.c. of the colloidal solution of arsenious sulphide were taken and coagulated with 50 c.c. of M/10 solution of barium chloride, this amount being the minimum quantity required to produce immediately the "sign of turbidity" corresponding to complete coagulation. The supernatant liquid was removed by decantation and the whole of the precipitate was transferred to the elutriating vessel. The apparatus was then put into operation and different fractions of the particles were collected at various velocities. These fractions were separately analysed. The method of analysis used for arsenic was the well-known iodometric method. This method did not give satisfactory results. At this time there appeared a paper[1] in which the defects of this method were pointed out and also some precautions given to counteract these. But not being satisfied with the results obtained even with the observation of these precautions another method by Kessler[2] which gave us quite concordant results was taken up. This method is also applicable in estimating antimony.

The various fractions obtained in the case of antimony sulphide sol with different electrolytes are as given in the following Tables.

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[1] Analyst. August (1922).

[2] Pogg. Ann., 118, 17 (1863).

Table III

500 c.c. of Antimony Sulphide sol coagulated with M/1 Sodium Chloride Solution.

Nozzle Head.	Equivalent quantity of Sb_2O_3 present in the fraction.	Velocity of water in the elutriator.
Nozzle I.		
3.8 c.m.	0.127 gm.	4.5 cms./min.
81.7 "	0.885 "	11.0 "
126.0 "	0.131 "	13.5 "

Table IV

500 cc. of Antimony Sulphide coagulated with 50 c.c. of M/10 Barium Chloride.

Nozzle Head.	Equivalent quantity of Sb_2O_3 present in the fraction.	Velocity of water in the elutriator.
Nozzle I.		
4.5 cm.	0.087 gm.	4.6 cms./min.
22.0 "	0.011 "	6.6 "
80.0 "	0.079 "	10.9 "
90.0 "	0.022 "	11.5 "
Nozzle III.		
40.3 cm.	0.397 "	25.7 "
50.0 "	0.513 "	28.0 "

Table V

500 c.c. of Antimony Sulphide coagulated with 1.3 gm. of Aluminium Chloride in Solution.

Nozzle Head.	Equivalent quantity of Sb_2O_3 present in the fraction.	Velocity of water in the elutriator.
Nozzle I.		
35.5 cm.	0.513 gm.	7.9 cms./min.
8.9 "	0.126 "	11.4 "
Nozzle III.		
90.0 cm.	0.065 "	37.1 "
130.0 cm.	0.307 "	41.8 "

Similar fractions were obtainable in the case of arsenious sulphide hydrosol.

Colloidal Solution of Manganese Dioxide

500 c.c. of the colloidal solution of Manganese Dioxide prepared in the manner described above were coagulated with sodium chloride, barium chloride, and aluminium chloride solutions respectively. In all the three cases it was found that the coagula consisted of only one size of particles and the results are shown in Table VI.

TABLE VI

Precipitating Electrolyte.	Quantity of the electrolyte used.	Piezometer Head	Nozzle Number	Elutriatioh Velocity
Sodium Chloride.	50 c.c. M/1 solution.	129 cms.	II.	13.85 cms./min.
Barium Chloride	50 c.c. M/10 solution.	66.5 "	III.	31.4 "
Aluminium Chloride	.3 0 gm.	125.5 "	III.	41.2 "

The above results were surprising and it was thought that these extraordinary results might be due to the fact that the original colloidal solution consisted of only one size of particles. It was, therefore, considered necessary to verify the conclusion on colloidal solutions of one size of particles only. Recourse was taken to ultra-filtration after the manner of Bechhold and the results obtained are shown in Tables VII-VIII:—

TABLE VII

Copper Ferrocyanide Sol after Ultra-filtration.

Precipitating Electrolyte	Piezometer Head	Nozzle Number	Elutriation Velocity
Sodium Chloride	3.2 cm.	II.	4.8 cm./min.
Barium Chloride	57.0 cm.	II.	9.95 cm./min.
Aluminium Chloride	91.4 cm. (?)	II.	12.0 cm./min.

TABLE VIII

Antimony Sulphide sol after Ultra-filtration

Precipitating Electrolyte	Piezometer Head	Nozzle Number	Elutriation Velocity
Sodium Chloride	6.1 cm.	II	5.4 cms./min.
Barium Chloride	65.9 "	II	10.5 "
Aluminum Chloride	0.7 "	III	14.5 "

Conclusion

A close examination of the results of elutriation shows that an interesting relationship exists between the precipitating electrolytes and the sizes of the particles in the coagula. In the case of sols of one size of particles only the ratio between the elutriating velocities for the particles of the coagula obtained by mono-, bi-, and trivalent electrolytes are as 1:2:3. In case of coagula obtained from colloidal solutions having more than one size of particles and giving a series of graded fractions on elutriation, the above ratio still holds good when the largest elutriation velocities alone are compared. The results are shown in Table IX for the sake of closer comparison.

It is evident from these results that the valency of the precipitating electrolyte is an important factor in determining the size of particles formed in their precipitation. In the case of a spherical particle falling freely in a viscous

TABLE IX

Colloidal solution	Elutriation velocities for various electrolytes.			Velocity ratios.	Remarks.
	Sodium Chloride	Barium Chloride	Aluminium Chloride		
Antimony Sulphide.	13.5 cms./Min.	28 cms/Min.	41.8 cms./min.	1:2.07:3.09	Cf. Tables III, IV and V, largest elutriation velocities alone compared.
Manganese Dioxide.	13.9 "	31.4 "	41.2 "	1:2.20:3	Cf. Table VI.
Copper Ferrocyanide	4.8 "	9.95 "	12 (?) "	1:2.07:(?)	Cf. Table VII. Ultra-filtered.
Antimony Sulphide.	5.4 "	10.58 "	14.5 "	1:1.96:2.7	Cf. Table VIII. Ultra-filtered.

liquid the velocity of fall which corresponds to the elutriation velocity is proportional to the square of the radius, that is, the surface of the particle. If we can assume that the elutriation velocities in the case of coagula are proportional to their surfaces these results will have more than an empirical importance. It would appear that the magnitude of the electrical charge present in the precipitating ion would determine the surface of the ultimate particles formed as a result of coagulation.

Summary

1. It has been shown that the elutriator can be used for grading the sizes of the particles present in a coagulum. Concordant results have been obrained by using a special adaptation of this instrument.

2. It has been shown that the largest elutriation velocities required to separate the final size of particles in coagula formed by precipitating the colloidal solution by mono-, di-, and trivalent electrolytes are approximately in the ratio of 1:2:3.

3. This provides a new evidence in favour of the electrical adsorption theory of coagulation of colloids.

4. It has been shown that colloidal solutions containing one size of particles form a single size only in the coagulum also.

5. Further experiments with the object of throwing light on the phenomenon of coagulation are in progress on the lines indicated above and it is hoped that a physical explanation of the interesting relationships so far observed will be forthcoming.

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THE ULTRA-VIOLET ABSORPTION SPECTRUM OF FURFURAL

BY FREDERICK H. GETMAN

The absorption of ultra-violet radiation by furfural was first studied by Hartley and Dobbie[1] in the course of an investigation of the absorption spectra of various heterocyclic compounds. Having prepared a highly purified sample of furfural, (B.p. 161°-161.5° at 764.9 mm.) they determined the absorption produced by varying thicknesses of an alcoholic solution containing 0.096 gram, or 1 milligram-molecule, of furfural, $C_5H_4O_2$, in 20 cc. of solvent. The following table gives the wave-lengths expressed in micro-millimeters, $\mu\mu$, where general absorption was found to commence.

TABLE I

Thickness in mm.	λ	$1/\lambda$
25	372.3	268.6
20	346.7	288.4
15	346.7	288.4
10	339.9	294.2
5	325.0	307.6
4	325.0	307.6
3	314.1	318.3
2	308.7	323.9
1	308.7	323.9

From these results they concluded that alcoholic solutions of furfural exhibit strong general, but no selective absorption.

Some years later, in a comparative study of the absorption spectra of a series of heterocyclic compounds as vapors, as liquids and in solution, Purvis[2] re-examined alcoholic solutions of furfural and found, contrary to the statements of Hartley and Dobbie, that a N/1000 solution exhibits marked selective absorption, the head of the band occurring at $\lambda 270\mu\mu$.

In view of these contradictory statements it appeared to be of interest to re-investigate the behavior of furfural toward ultra-violet radiation in both alcoholic and aqueous solutions.

A Hilger quartz spectrograph (size E6) with a wave-length scale was used in making the spectrograms. As a source of ultra-violet radiation a condensed spark between two electrodes, made of alloys of ferro-vanadoum and ferro-chromium respectively, was used. This combination was found by the author several years ago[3] to give an unusually large number of closely spaced lines many of which are characterized by exceptional brilliance. It has proven so

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[1] Hartley and Dobbie: J. Chem. Soc. 73, 598 (1898).

[2] Purvis: Ibid. 97, 1655 (1910).

[3] Getman: J. Phys. Chem. 25, 150 (1921).

satisfactory that he ventures here to reiterate its merits as a source of ultraviolet radiation.

The furfural was prepared and purified according to the procedure outlined in a previous paper[1] treating of the electrical conductance of various salts dissolved in furfural. The ethyl alcohol used was prepared by refluxing 95 per cent alcohol over lime and subsequently distilling, while in the preparation of the aqueous solutions, so-called "conductance water" was used.

In each series a mother solution containing 0.96 gram of furfural in 100 cc. of solvent, i.e. a N/10 solution, was prepared by direct weighing, and from this N/100 and N/1000 solutions were prepared by dilution.

It should be pointed out that N/10 aqueous solutions of furfural are perfectly homogeneous, it having been shown by Mains[2] that separation into two layers does not occur until a concentration of about 8 percent by weight of furfural is reached.

The solutions were examined in a "Baly tube" provided with a 10 cm scale graduated in millimeters. The thickness of the absorbing layer was diminished step by step until complete transmission was secured. The time of exposure was uniformly 10 seconds throughout the entire series of experiments.

The limits of absorption in both the alcoholic and aqueous solutions were found to be identical. It is probable that, with a spectroscope of greater dispersive power, the limits of absorption in the alcoholic solutions would be found to lie nearer the visible portion of the spectrum in accordance with the law enunciated by Kundt that the limits of absorption of a solute are pushed toward the red region of the spectrum as the refractive index of the medium is increased. The limits of absorption in N/10 and N/100 solutions, together with the corresponding values found by Hartley and Dobbie, and Purvis, are given in the following table.

TABLE II

(N/10 solution)

Thickness in mm.	λ (G)	λ (H & D)	λ (P)
30	. . .	. . .	359
10	345	347	. . .
2	. . .	325	213
1	316	311	. . .
	(N/100 solution)		
30	. . .	. . .	316
10	316	309	. . .
2	. . .	. . .	297
1	300	. . .	. . .

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[1] Getman: J. Phys. Chem. 28, 212 (1924)

[2] Mains: Chem. and Met. Eng. 26, 779 (1922).

The spectrograms of N/1000 furfural solutions were found to reveal, in addition to general absorption, the existence of a well-defined and persistent band. The absorption curve corresponding to this band is plotted in Fig. 1 together with that determined by Purvis, the former being the full line curve and the latter the dotted. It is apparent that the two curves are essentially identical, the differences being no greater than the probable experimental errors of the method. The position of the head of the absorption band is the same in each, viz., λ270μμ, or frequency 370.

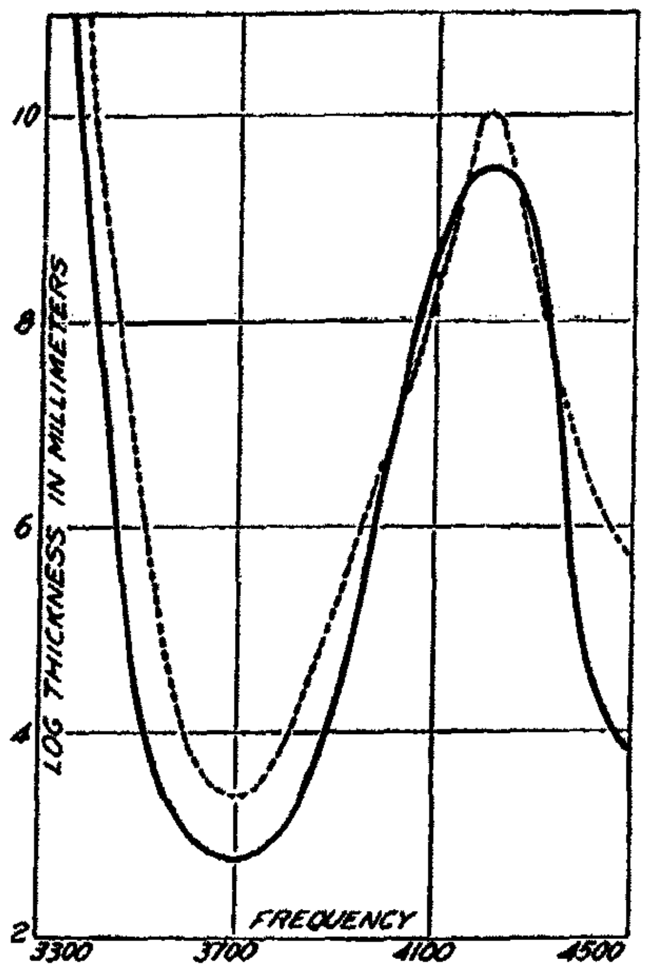


Fig. 1

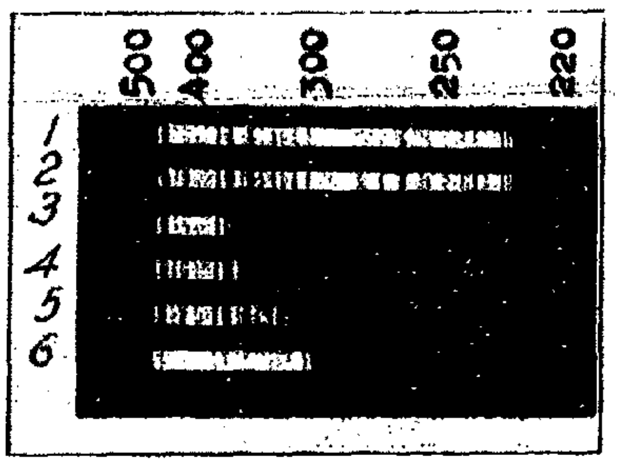


Fig. 2

The marked absorbing power of minute quantities of furfural for ultraviolet radiation is further brought out by the spectrogram shown in Fig. 2, where the six successive spectra have the following significance: (1) spectrum of source, (2) absorption spectrum of 50 mm. of solvent, (3), (4), (5) and (6) absorption spectra of solutions of furfural containing 1 part of solute in 100, 1000, 10,000 and 100,000 parts of solvent respectively. It will be seen that only in the last and most dilute solution are the shorter wave-lengths transmitted. It is undoubtedly to the persistence with which furfural absorbs ultra-violet radiation that we must attribute Hartley and Dobbie's failure to discover its selective in addition to its general absorption.

Although freshly distilled furfural is almost colorless, it develops color on exposure to light, or on prolonged standing, passing from a pale straw-colored liquid, through various shades of yellow and orange to a dark brown liquid which is almost opaque to light. It seemed of interest to ascertain whether, as the visible absorption spectrum of furfural changes, a corresponding change takes place in its ultra-violet absorption spectrum. In order to settle this point, a flask containing a sample of pure and nearly colorless furfural was exposed to the direct rays of the sun for two weeks, at the expiration of which time the liquid had acquired a deep amber color. A series of aqueous solutions were prepared from this substance and their ultra-violet absorption spectra examined in the manner already described. It was found that the deep band in the N/1000 solution remained unaltered, but that in the more concentrated solutions the general absorption was greater than in corresponding solutions of freshly distilled furfural. This is shown in the following table where the comparative values of the limits of absorption of varying thicknesses of N/10 solutions of the pure and yellow modification of furfural are given.

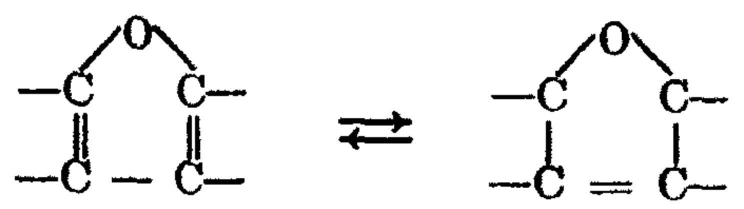
Table III

(N/10 solution)

Thickness in mm.	*(Pure)*	*(Yellow)*
100	370	420
50	370	396
10	345	348
5	335	335
1	316	316

In other words, exposure to light appears to cause an increase in the absorption in the more concentrated solutions in the direction of the longer wave-lengths, the yellow color being due to the selective absorption of the violet and a portion of the blue region of the visible spectrum. It seems highly probable that the instability of furfural as shown, by its tendency to polymerize, is intimately connected with its marked absorbing power for ultra-violet radiation.

If it be true, as the advocates of the theory of dynamic isomerism maintain, that no organic compound shows an absorption band unless the possibility of tautomerism exists within the molecule, the existence of selective absorption in furfural might be explained by an isorropic process such as is represented by the following formulas:



This, however, is purely conjectural and no satisfactory explanation of the existence of an absorption band in furfural or other organic compounds can be advanced until a rational theory of the absorption of radiation has been developed. In this connection it is of interest, however, to note that Baeyer[1]

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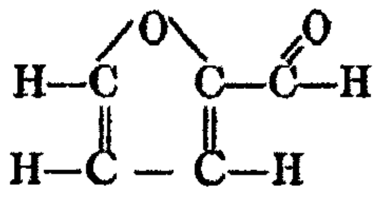
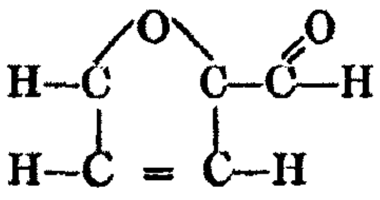
[1] Ber. 10, 1358 (1877).

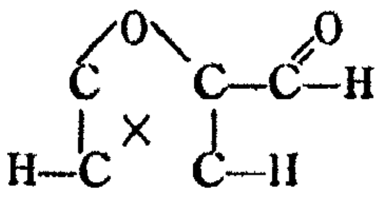
as the result of his study of the chemical behavior of furfural, advanced three possible structural formulas of the compound, as follows:



(1)



(2)



(3)

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THE PURIFICATION OF INSULIN AND SIMILAR SUBSTANCES BY SORPTION ON CHARCOAL AND SUBSEQUENT RECOVERY[1]

P. J. MOLONEY, AND D. M. FINDLAY

"Since the adsorption of liquids by solids is selective it follows that one liquid will be adsorbed more by a solid than will a second liquid and that consequently the first will displace the second from contact with the solid. No systematic study of this phenomenon seems to have been made[2]." The same is true for the sorption of solutes[3] or colloids from solution and it seems likely that systematic study of the latter cases would lead to valuable improvements in the technique of chemical purification. Many chemically ill-defined substances—dyes, toxins, etc.,—are readily removed from solution by shaking with charcoal or kaolin; if they could as readily be recovered from the sorber they would be accessible to chemical investigation.

Comparatively little experimental work has been published on the separation of sorbate from sorber; in connection with our endeavors to purify insulin by means of charcoal we have been led to classify the available methods into four main groups. Methods of the first group are applicable whether the sorption is reversible or not. Those of the other three only when it is at least approximately reversible.

GROUP I: *By chemical action on the sorber*, for instance:—

(A) by dissolving it, leaving the sorbate undissolved. Pepsin[4] and lipase[5] have been purified by sorption on cholestrin followed by solution of the latter in ether; similarly insulin[6], by sorption on benzoic acid and subsequent treatment with ether.

(B) If a complex containing an amorphous sorber were kept under such conditions that crystallization set in, the sorbate would no doubt in many cases be released; Freundlich and Schucht[7] showed that amorphous mercuric sulphide sorbs more dye than the crystalline form into which it spontaneously changes, but we have found no case of isolation or purification by this method.

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[1] From the Insulin Division, Connaught Laboratories, University of Toronto.

[2] Bancroft: "Applied Colloid Chemistry", p. 72, (1921).

[3] For the sake of brevity the word "solution" "solute", and "solvent" are employed to include colloidal suspensions, etc.; this avoids the continuous repetition of such terms of "solution or suspension", "solute or suspensoid", "solvent or dispersoid." The word "complex" is used as an abbreviation for "sorber plus sorbate."

[4] E. Brücke: Virchow's Archiv. 25 279.

[5] Willstätter: Hoppe-Seyler's Z. physiol. Chem. 125, 191 (1923).

[6] J. Biol. Chem. 57, 359 (1923).

[7] Z. physik. Chem. 85, 660 (1913).

(C) Finally if further study should show that the phosphate solutions used by Willstätter[1] convert alumina or kaolin into a phosphate incapable of sorbing enzymes, his method of purifying the latter would come into this group.

Group II: *By changing the temperature,* effecting the sorption at a temperature where the sorption coefficient is high and the removal at a temperature where it is low. This method has found wide application in the case of gases. Effront's[2] measurements of the effect of temperature on the sorption of ptyalin by filter paper might lead to a method of purifying the ptyalin if anything like equilibrium was reached in his experiments. This method is of general applicability and can be used in conjunction with those of the other groups.

Group III: *By lowering the chemical potential of the solute in the solution.* This may be effected:—

(A) by lowering its concentration, as by repeatedly washing the complex with fresh portions of the original solvent; e.g., the removal of sorbed sugar[3] from charcoal by washing with water. Because of the general form of the sorption isotherm this method must be expected to give a poor yield and a very dilute solution of the product desired; it has been employed however by Effront,[4] who purified pepsin by sorption on filter paper and washing out with water.

(B) by adding to the original solvent some fourth substance and thus in effect creating a new solvent in which the sorbate is more soluble than in that from which it is sorbed. Acids for instance, sorbed by wool[5] from aqueous solution, may be recovered by digestion with dilute alkali; to recover the original acid of course requires a subsequent operation. Changing the pH of the solution from which a colloid has been sorbed might have the same effect. Ambard[6] and Effront[7] used dilute solutions of starch to remove amylase from starch granules and ptyalin from cellulose respectively, but did not recover the enzymes in the pure state.

(C) by the use of an entirely new solvent, e.g., iodine or methyl violet[8] taken up by charcoal from aqueous solution may be recovered by treating the complex with alcohol.

Group IV: *By replacing the original sorbate by another.* This may be effected by digesting the complex with a solution, (or suspension) of some fourth substance which is readily sorbed and which does not itself carry the

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[1] Hoppe-Seyler's Z. physiol. Chem.

[2] Compt. rend. Soc. Biol. 86, 271.

[3] Bayliss: "Principles of General Physiology" 2nd Ed. p. 69.

[4] Compt. rend. Soc. Biol. 87, 128.

[5] Von Georgievics: Monatsh. f. Chem. 32, 655 (1911).

[6] Bull. Soc. Chim. Biol. 3, 51-56.

[7] Compt. rend. Soc. Biol. 86, 271.

[8] Bancroft: "Applied Colloid Chemistry, p. 113 (1921).

original sorbate into the interface.[1] Saponin[2] has been used to prevent rennet from concentrating in the foam of a shaken solution, and it has also been used to re-activate[3] rennet sorbed on charcoal; Freundlich and Kaempffer[4] observed that the sorption of uranium salts is decreased by the addition of thorium salts, benzoic acid, strychnine nitrate, etc., to the solution, and ascribed this to replacement of the uranium in the complex by these substances; but we have found no clear case of isolation and purification by replacement in the complex. However, since the boundary between groups I-C and IV is ill-defined, it may be that some Willstätter's[5] work on the purification of enzymes comes under this head.

Although hitherto they have been but little used, we believe that the systematic application of the methods of the fourth group is the best means available for isolating and purifying the chemically ill-defined substances so important from the physiologist's point of view; it does not seem too much to hope that by their means a technique of practical sorption and recovery may be developed which will play the same part in the purification of colloids that fractional distillation and fractional crystallization play in the purification of volatile and crystalline chemicals.

Application to the Purifcation of Insulin

In our work charcoal is used as a sorber, about one milligram being needed to remove the insulin from 1 cc. of a relatively pure solution such as the clinical product.[6]

The methods of Group I are inapplicable with charcoal as a sorber; as stated above they gave us good results with benzoic acid. Method II was used in combination with the others; III-A (washing with water), proved useless. Under III-B come our attempts to recover the insulin by digesting the complex with aqueous solutions of varying pH—from hydrochloric acid of pH 1.0, to borate and phosphate buffers as alkaline as pH 9.8; negative results were obtained in every case, while greater alkalinity destroys the insulin. Experiments in which the complex was digested with various solvents[7] of insulin—phenol, glacial acetic acid, or a mixture of hydrochloric acid and alcohol—come under III-C; the results here too were disappointing.

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[1] Hunter (J.Chem. Soc. 23, 73 (1870)) has shown that the sorption of ammonia from gases by charcoal is increased by the presence of sorbed water.

[2] S. and S. Schmidt-Neilson: Hoppe-Seyler's Z. physiol. Chem. 68, 317 (1910)

[3] Jahnson-Blohm: Hoppe-Seyler's Z. physiol Chem. 82, 178 (1912).

[4] Z. physik. Chem. 90, 681 (1915).

[5] Hoppe-Seyler's Z. physiol. Chem. 125, 132 (1923).

[6] With a crude solution of insulin much larger amounts of charcoal are needed, due no doubt to the sorption of other constituents of the crude preparation. One might expect with Freundlich that constituents which lower the surface tension of the solution would be preferentially sorbed; this conclusion is borne out by the following stalagmometer readings obtained with a crude solution of insulin after digestion with varying amounts of charcoal:—

Grams charcoal.	0.0	0.2	0.4	0.6
Drops of solution	83	79	75	72

[7] Moloney and Findlay: Trans. Roy, Soc. Canada, 17, Sec. V, 77 (1923).

Our first successful results were obtained by the method of Group IV, viz; by leaching a complex containing four units of insulin with 0.3 N solutions of fatty acids in aqueous alcohol, the fatty acid was removed by extraction with ether and the aqueous solution injected into rabbits.[1] The table gives the blood sugar readings observed; from these it may be deduced that by means of lauric acid three quarters of the sorbed insulin has been recovered, about one quarter by caprylic and heptylic acids and very little by the others. A parallel series with the sodium salts showed a slight recovery with the laurate and none with the others.

	Blood Sugar	
	Normal	*2 hrs. after injection*
Butyric acid	0.118	0.104
Caproic	0.118	0.104
Heptylic	0.110	0.072
Caprylic	0.124	0.072
Lauric	0.118	0.054 (convulsions).

[2]There can be little doubt that the removal of the insulin is due to its replacement by the fatty acid. In the first place Bartell and Miller[3] have shown that in soap solutions it is the acid liberated by hydrolysis which is sorbed by charcoal. This accounts for the greater efficiency of the acids compared with their salts in the recovery of insulin. Then the same authors have shown that the higher fatty acids are more readily sorbed by charcoal than the lower and our results show that their ability to liberate insulin increases in the same direction.[4] Finally our experiments with alcoholic solutions of oleic acid, stearic acid, sodium oleate and castille soap gave results as good or better than those with lauric acid, while by the use of benzoic acid or of salicylic acid (which according to Bartell and Miller are very strongly sorbed by charcoal) practically all the insulin can be recovered. Glycocoll, (not sorbed by charcoal) tartaric acid (sorption about the same as butyric), hydrochloric, nitric or sulphuric acids (sorption less than acetic), gave no yield, as was to be expected; the same is true of citric acid, alanine, potassium iodide and potassium nitrate. Phenol gave no yield, but an alcoholic solution of thymol recovered 75%, and so did an aqueous solution of ammonia, which is strongly sorbed by charcoal and a solution of bile salts whose power to greatly decrease the surface tension of aqueous solutions has long been known.

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[1] Caution must be observed in interpreting the results of such experiments, to avoid the use of reagents which themselves lower blood sugar, such for example as sodium dihydrogen phosphate, potassium iodide, guanidine sulphate (Collip: J. Biol. Chem. 1923.

[2] We found that the dyes methylene blue, safranin and methy violet, which are readily sorbed by charcoal may be recovered by the use of soap solutions. In the case of the last two named the acidity of the solution from which the dye was sorbed does not affect its subsequent recovery; but if methylene blue be sorbed from solutions of pH 2.2 (phthalate buffer) it cannot be removed by aqueous soap solutions, while if sorbed at pH 3.8 part at least can be recovered.

[3] J. Am. Chem. Soc. **45**, 1106 (1923)

[4] Warburg's work shows that in other instances the higher members of a series are the better replacing agents. (Z. Elektrochem, **28**, 70 (1922)).

The following process based on the experiments referred to above has proved successful in the manufacture of commercial Insulin in these Laboratories[1]:—Ten litres of a partially purified solution of insulin are set at pH 2.5 with hydrochloric acid and left overnight with 400 grams of charcoal with occasional stirring.[2] The charcoal is then removed, washed with water, and stirred with two litres of a 5% solution of acetic acid in 60% alcohol—this reagent leaches off certain impurities but leaves the insulin. After filtration the charcoal is digested for several hours at room temperature with 3.5 litres of a 12% solution of benzoic acid in 60% alcohol, and the insulin recovered from the solution by evaporating off the alcohol and removing the benzoic acid by ether—after which treatment of course the ether remaining dissolved in the insulin solution must be got rid of by evaporation. We are at present employed in studying the effect of higher temperatures during sorption and recovery; it appears that thereby the time required for the various processes can be materially reduced.

As it seemed likely that reagents which replace insulin from its complex with charcoal might also replace it from its complex in the pancreas, we tried extraction of the glands with alcoholic solutions of benzoic acid and obtained yields up to 2,000 units per pound of gland.[3] Parallel runs with N/20 sulphuric acid (the reagent used by Doisy, Somagyi and Schaffer[4]) gave only 100-300 units per pound; and in the light of our experiments with charcoal cited above it seems probable that most of this must be ascribed to the action of the fatty acids liberated by the sulphuric from the gland.

The paper presents a classification of the methods available for recovering adsorbed substances from charcoal, etc., with a view to their isolation and purification; gives instances gathered from the literature of their application for such purposes and details their use in the purification of insulin.

Our thanks are due Professor W. Lash Miller for assistance in putting this paper in form.

University of Toronto,
Connaught Laboratories,
December, 1923.

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[1] Best and Scott: J. Biol. Chem., 57, 709 (1923).

[2] If charcoal be used on an insulin solution which is deteriorating, the rate of destruction is increased.

[3] The crude product so obtained is very unstable; methods of purifying it further are being studied.

[4] Proc. Am. Soc. Biol. Chem. Toronto meeting, December, (1922).

NEW BOOKS

Light and Colour. *By R. A. Houstoun. 22×15 cm; pp. xi+179. New York and London: Longmans, Green and Co., 1923. Price: $2.50.* The publisher's advertizement says that "this book is intended for the general reader and deals with the spectrum, the nature of light, colour photography, and allied subjects. The treatment, though popular, is everywhere from the most modern standpoint." This statement is unnecessarily modest for the book can be read with profit by any scientific man. My attention was first called to the book by Professor Eve of McGill University, who told me that he had enjoyed it. I am glad to bear witness that I have both enjoyed and profited by it.

The chapters are entitled: Newton and the colours of the spectrum; the nature of light; invisible rays; applications to the structure of atoms and stars; the primary colours; colour blindness; colour photography and stereoscopy; the light of the future: photochemistry and allied effects; phototherapy; the psychology of colour.

There is a distinctly interesting diagram of the rainbow, p. 5. and it is certainly worth while to quote the views on color of Dr. Barrows, who was Newton's predecessor in the Lucasian professorship of mathematics. "White is that which discharges a copious light equally *clear in every direction. Black is that which does not emit light at all*, or which does it very sparingly. Red is that which emits a light more clear than usual, but interrupted by shady interstices. Blue is that which discharges a rarefied light, as in bodies which consist of white and black particles arranged alternately. Green is nearly allied to blue. Yellow is a mixture of much white and a little red; and purple consists of a great deal of blue mixed with a small portion of red. The blue colour of the sea arises from the whiteness of the salt it contains, mixed with the blackness of the pure water in which the salt is dissolved; and the blueness of the shadows of bodies, seen at the same time by candle and daylight, arises from the whiteness of the paper mixed with the faint light or blackness of twilight."

Houstoun adopts the view of Edridge-Green in regard to the presence of indigo in the spectrum. "Dr. Edridge-Green states that Newton had exceptionally good colour vision, and that he saw a difference in the spectrum at this point which was not visible to the average man. According to Edridge-Green's classification of colour vision the average man sees only six colours in the spectrum, red, orange, yellow, green, blue, and violet. He consequently refers to normal colour vision as hexachromic. . . . The average man sees, of course, intermediate shades between these colours, but these six colours appear to be fundamental. But there are certain individuals, the seven-colour class or hepta-chromic according to Edridge's-Green's terminology, who see a seventh colour, indigo, between the blue and the violet. They have a decidedly better colour perception than the hexachromic. It is not merely a matter of colour nomenclature; the heptachromic really see something at this region in the spectrum, which the hexachromic do not see. Newton, according to Edridge-Green, was a heptachromic."

Edridge-Green states that only about four in a thousand have heptachromic vision; but Houstoun found three cases out of eighteen observers taken at random, p. 9. These three all objected to the word indigo, and chose dark blue as a more suitable name; they all said it was more like blue than violet. They placed the boundary between blue and indigo at $465\mu\mu$. Another, and perhaps the real, reason why Newton included indigo was because this made seven colors and brought his phenomenon in line with the doctrine of the music of the spheres, p. 17, according to which the sun and moon and the five planets, Saturn, Jupiter, Venus, Mars, and Mercury, emitted musical notes as they revolved in their orbits, thereby producing a heavenly harmony. "The music of the spheres forms a curious bypath in the history of human thought. And yet not altogether a bypath, for it inspired Kepler to discover the third law of planetary motion, and upon this law Newton built his theory of gravitation."

"It will be noticed in the above scheme that the sun and moon are included in the number of the planets. This was the teaching of the priest-astronomers of the early Babylonian civilisation. Uranus and Neptune were, of course, not discovered then. The seven planets were regarded as gods, an idea that lingered on into medieval times in astrology; the sun's influence on the crops and weather was, of course, very obvious, and it became natural to assume that the other planets exerted an influence on human affairs, less obvious perhaps, but nevertheless very important. To a primitive pastoral people, often abroad at night under a clear tropical sky, the planets would naturally appear very mysterious moving on their regular paths among the stars. The division of the month into weeks was instituted in their honour, an arrangement still in use in this country with the names of the Scandinavian deities substituted. It was doubtless owing to there being seven planets, that the number seven acquired the sacred character it has in the Bible, that there were seven important metals in alchemy, that there were seven notes in the octave, and seven colours in the spectrum," p. 19.

"On p. 71 there is a discussion of the effects of mixing coloured lights. "The red required for our experiment must be a pure red without any tint of orange, somewhat similar to the red of the railway signal lamps; the green must contain neither yellow nor blue, and must be purer than the green of the signal lamps; the blue must be an ultramarine with a good deal of violet in it. Under these circumstances if the red is superimposed on the green we obtain yellow. Strong red imposed on weak green gives orange, weak red on strong green yellowish green. Green superimposed on blue gives peacock blue. Red superimposed on blue gives magenta, and red on a stronger blue gives purple. Red, green, and blue superimposed on one another make white. If white is dimmed, we get gray; if orange is dimmed we get brown. Superimposing white on any colour makes it paler. Thus by means of the three colours, red, green, and blue, we obtain nearly all the colours that occur in nature. They do not give us violet, but pure violet does not occur frequently in nature. So red, green, and blue are termed the primary colours. . . .

"Peacock blue, magenta, and yellow are termed the three complementaries, since each of them combined with one of the primaries gives white. Peacock blue is sometimes referred to as minus red, since it is the colour obtained by subtracting red from white, and in the same way magenta and yellow are referred to as minus-green and minus-blue.""

"So far we have dealt with adding or mixing coloured lights. We have now to consider the mixture of coloured pigments. This is a subject with which to a certain extent we are all familiar, owing to our experience with water colour paint-boxes when children. We then learned that approximate representations of all colours could be produced by mixing red, yellow, and blue, or more accurately, crimson, yellow, and peacock blue, *i.e.* the three complementaries on the colour diagram. For crimson and yellow mixed in varying proportions gave red and orange, yellow and blue gave green, and blue and crimson mixed in varying proportions ultramarine-blue and the purples. Hence these colours have been termed by the artists the primary or elementary colours, for human nature has had a natural tendency to think in terms of elements, especially in medieval times; some painters have restricted themselves to the use of these three colours, adding black for the purpose of darkening them and obtaining the browns and greys, although they would undoubtedly have obtained a better representation of the hues of nature, if they had used other colours as well.

"If we desire to renew our studies in mixing coloured pigments, then we can go back to the crimson lake, gamboge, and Prussian blue of the water colour paint-boxes. Or we may use instead Arnold's waterproof inks, carmine, yellow, and Prussian blue, which give more intense colours. If we wish to exhibit the mixing of pigments to a large audience, the best method is to get six glass cylinders, fill the first with a crimson liquid, the second with a yellow liquid, and the third with a blue liquid, and then pour the liquids together into the fourth, fifth, and sixth to make orange, green, and purple. The glasses should be held before a well-lighted white background. Fuchsin, naphthol yellow, and copper sulphate are suitable colours to use.

"If we add yellow and blue pigments we get green. If we add yellow and blue lights we get white. Whence comes the contradiction?

"A yellow pigment appears yellow because, when the constituents of white light fall upon it, the blue and violet are absorbed, and red, yellow, and green reflected. Most yellows occurring in nature are not very pure, and reflect red and green as well as yellow. A blue pigment appears blue because it absorbs red and yellow, most blues occurring in nature are not very pure, and reflect green as well as blue. When the yellow and blue pigments are mixed, the mixture absorbs all the colours absorbed by its components singly, *i.e.*, blue, violet, red, and yellow. Green is the only colour left. It alone is reflected and the mixture appears green. A mixture of pigments gives only the colour which neither absorbs, not the sum of the two colours, as we obtain when adding lights," p. 75.

"Dalton was first distinctly convinced of his peculiarity of vision in 1792, when he was 26 years of age, by the discovery that the flower of a geranium which appeared to others pink in all lights, appeared to him blue by day, and what he called red by candle light. All his friends except his brother said there was not any striking difference in the colour by the two lights. This observation led him to examine the peculiarities of his vision; he then found that the pure colours, red, orange, yellow, and green were practically all alike to him, and that he called them all yellow, but that he could distinguish blue and purple, and that he called these colours by the correct names. Dalton said that blood appeared bottle-green to him, grass appeared very little different from red. A laurel leaf was a good match for a stick of sealing wax," p. 87.

"Put in its simplest form the Young-Helmholtz theory states that in the retina of each eye there end three sets of nerves, one set for the sensation of red, another for the sensation of green, and a third for the sensation of blue. When red light falls on the eye, it stimulates the red nerves. When yellow light falls on the eye, it stimulates both the red and green nerves. When white light falls on the eye, it stimulates all three sets of nerves. The colour blind lack either one or two sets of nerves. If they lack two, they are totally colour blind, and are referred to as monochromats. If they lack one set, they are referred to as dichromats; all the commonly occurring cases are dichromats who lack either the red or green set of nerves, and are consequently referred to as red or green blind. Observers with normal colour vision are referred to as trichromats.

"One objection to the Young-Helmholtz theory is that there is no anatomical evidence for the three sets of nerves, but the most serious objection is, that the colour blind do not fit into the original classification. I have tested carefully some thirty colour blind individuals, and not one of these agreed with Helmholtz's typical cases. Helmholtz became aware of the inadequacy of his earlier views, and before his death he modified his theory so as to make it better able to take account of the cases occurring in practice. But when the theory is modified, it loses its original simplicity and force.

"The other theory most prominently before the public at present is the non-elemental theory which has been advocated by Dr. Edridge-Green for the past twenty years. According to this theory there are no elementary sensations; colour vision occurs in all degrees of goodness passing in insensible gradations from the totally colour blind through the normal to those who have better colour vision than the normal, and the colour blind should not fall into classes like the red-blind and greenblind.

"It should be stated that the mathematical development of Helmholtz's modified theory does equally well for the non-elementary theory, so that there is no serious difference between the two standpoints; the current practice of identifying Helmholtz's name with his earlier view is hardly fair to his memory, in consideration of the great advances he made in the study of the subject," p. 90.

"The bead test reveals not only colour blindness, but differences in the classification of colours. Some people are very particular, and put only a pure red in the red hole; others include pink and crimson under red, and a few are inclined to extend the term to include brown and amber. Usually out of four men two put peacock blue in blue and one puts it in green, while the fourth leaves it in the drawer. Three out of four women put peacock blue in blue. Such differences interest the people using the test very much; in fact I have heard the apparatus called "The Parlour Game Test for Colour Vision." and it is really more interesting than many parlour games. In using it the examiner must distinguish between a selection made because the examinee sees the colours different and a selection made because he classifies them differently; this is, however, easy," p. 93.

"The best known name in the region of phototherapy is that of Professor Finsen of Copenhagen, who worked for many years on the subject, from 1893 onwards. He had an institute for phototherapy at which he treated large numbers of patients; he was fortunate in obtaining help both from private individuals and the state, and in thus being able to carry his plans to completion. He was awarded a Nobel Prize for his work. His chief success was with the skin disease lupus, a form of tuberculosis, of which he treated from 1,200 to 1,300 cases. It is stated that he obtained a cure or considerable improvement in between 90 and 94 per cent. of these cases. But his treatment is not much used in our own country at present, apparently because it is slow, tedious, and expensive," p. 148.

"There have been two schools of thought with reference to rickets. According to the one view the disease is due to a deficiency of a vitamin—the fat soluble vitamin A—which promotes growth. Vitamins are substances without the presence of a very small quantity of which the body is unable to derive the proper nourishment from its food. According to the other view the disease is due to confinement and defective hygiene. The two views are probably complementary, not contradictory. In many cases a course of cod-liver oil has been very successful, apparently because it supplied the lacking vitamin.

"It has been suggested that sunlight or ultra-violet light sets up inflammatory processes in the skin which produce vitamin A by a photochemical reaction. This would account for the seasonal prevalence of rickets in winter and early spring. The matter is, however, still very hypothetical," p. 150.

"Thus the mountain sunshine has a quality which the sunshine of the valleys and plains has not; it contains certain ultra-violet radiations which the latter lacks. At first sight 10 or 20 A. U. may not seem worth climbing the mountain for. But the fact that there are more of the limiting radiations at high altitudes means that more are being absorbed there; now the absorption of ultra-violet light is often accompanied by ionisation—*i.e.*, in this case by change in the electrical conditions of the atmosphere. This may make the air fresher. What exactly constitutes fresh air is not known. It is not merely sufficient to diminish the carbon dioxide content, as was formerly thought to be the case. Everyone admits that thousands of cubic feet of air may be pumped through a room and yet leave it with a close feeling. There are subtle changes in the condition of the molecules that defy chemical analysis, and yet conduce very much to our feeling of health. Possibly the radiations present in mountain sunshine and absent from ordinary sunshine may bring these changes about," p. 152.

In regard to the Cooper Hewitt lamp the author says, p. 154, that "the colour of the lamp was always against it; it gave everything a green, ghastly hue. Golden hair appeared a mossy green, a penny stamp was exactly the colour of a three half-penny one when illuminated by its rays, and I was told by some acquaintances, who worked temporarily during the war on the night shift in a factory illuminated by the mercury arc, that the first night they opened out their sandwiches, they simply looked at them in the green light, and then tied them up again; the colour was too much for them."

Wilder D. Bancroft

Dimensional Analysis. *By P. W. Bridgman. 23×16 cm; pp. 115. New Haven: Yale University Press, 1922. Price: $5.00.* "The growing use of the methods of dimensional analysis in technical physics, as well as the importance of the method in theoretical investigations, makes it desirable that every physicist should have this method of analysis at his command. There is, however, nowhere a systematic exposition of the principles of the method. Perhaps the reason for this lack is the feeling that the subject is so simple that any formal presentation is superfluous. There do, nevertheless, exist important misconceptions as to the fundamental character of the method and the details of its use. These misconceptions are so wide-spread, and have so profoundly influenced the character of many speculations, as I shall try to show by many illustrative examples, that I have thought an attempt to remove the misconceptions well worth the effort.

"I have therefore attempted a systematic exposition of the principles underlying the method of dimensional analysis, and have illustrated the applications with many examples especially chosen to emphasize the points concerning which there is the most common misunderstanding, such as the nature of a dimensional formula, the proper number of fundamental units, and the nature of dimensional constants. In addition to the examples in the text, I have included at the end a number of practice problems, which I hope will be found instructive."

Dimensional analysis and the principle of similitude are interchangeable terms, p. 10. "The purpose of dimensional analysis is to give certain information about the relations which hold between the measurable quantities associated with various phenomena. The advantage of the method is that it is rapid; it enables us to dispense with making a complete analysis of the situation such as would be involved in writing down the equations of motion of a mechanical system, for example, but on the other hand it does not give as complete information as might be obtained by carrying through a detailed analysis," p. 17.

"The dimensional formula need not even suggest certain essential aspects of the rules of operation. For example, in the dimensional formula of force as mass times acceleration, the fact is not suggested that force and acceleration are vectors, and the components of each in the same direction must be compared. Furthermore, in our measurements of nature, the rules of operation are in our control to modify as we see fit, and we would certainly be foolish if we did not modify them to our advantage according to the particular kind of physical system or problem with which we are dealing. We shall in the following find many problems in which there is an advantage in choosing our system of measurement, that is, our rules of operation, in a particular way for the particular problem. Different systems of measurement may differ as to the kinds of quantity which we find it convenient to regard as fundamental and in terms of which we define the others, or they may even differ in the number of quantities which we choose as fundamental. All will depend on the particular problem, and it is our business to choose the system in the way best adapted to the problem in hand.

"There is therefore no meaning in saying 'the' dimensions of a physical quantity, until we have also specified the system of measurement with respect to which the dimensions are determined. This is not always kept clearly in mind even by those who in other conditions recognize the relative nature of a dimensional formula," p. 24. The author holds that it is permissible, for instance, to make the dimensions of the temperature the dimensions of energy if that is compatible with the physical facts (and it seems to be) and if that seems advantageous.

"This view of the nature of a dimensional formula is directly opposed to one which is commonly held, and frequently expressed. It is by many considered that a dimensional formula has some esoteric significance connected with the 'ultimate nature' of an object, and that we are in some way getting at the ultimate nature of things in writing their dimensional formulas. Such a point of view sees something absolute in a dimensional formula and attaches a meaning to such phrases as 'really' independent, as in Riabouchinsky's comments on Lord Rayleigh's analysis of a certain problem in heat transfer. For this point of view it becomes important to find the 'true' dimensions, and when the 'true' dimensions are found, it is expected that something new will be suggested about the physical properties of the system. To this view it is repugnant that there should be two dimensional formulas for the same physical quantity. Often a reconciliation is sought by the introduction of so-called suppressed dimensions. Such speculations have been particularly fashionable with regard to the nature of the ether, but so far as I know, no physical discovery has ever followed such speculations; we should not expect there would if the view above is correct," p. 24.

"My point of view is essentially that precisely the same experience which is demanded to enable us to say whether a system is mechanical or electrical is the experience which is demanded in order to enable us to make a dimensional analysis. This experience will in the first place inform us what physical variables to include in our list, and will in the second place tell us what dimensional constants are demanded in any particular problem," p. 50.

"With regard to the dimensional formulas of dimensional constants, we may merely appeal to experience with the observation that all such constants are of the form of products of powers of the fundamental quantities. But it is evident on reflection, that any law of nature can be expressed in a form in which the dimensional formulas of the constants are of this type, by the device, already adopted, of introducing dimensional constants as factors with the measured quantities in such a way as to make the equation complete. We will therefore assume that the equations of motion (which are merely expressions of the laws of nature governing phenomena) are thrown into such a form that the dimensional constants are of this type; this is seen to involve no real restriction. It appears, therefore, that *dimensional analysis is essentially of the nature of an analysis of an analysis*," p. 52.

"We are to imagine ourselves as writing out the equations of motion at least in sufficient detail to be able to enumerate the elements which enter them. It is not necessary to actually write down the equations, still less to solve them. Dimensional analysis then gives certain information about the necessary character of the results. It is here of course that the advantage of the method lies, for the results are applicable to systems so complicated that it would not be possible to write the equations of motion in detail," p. 52.

"There are in engineering practice a large number of problems so complicated that the exact solution is not obtainable. Under these conditions dimensional analysis enables us to obtain certain information about the form of the result which could be obtained in practice only by experiments with an impossibly wide variation of the unknown arguments of the unknown function. In order to apply dimensional analysis we merely have to know what kind of a physical system it is we are dealing with, and what the variables are which enter the equation; we do not even have to write the equations down explicitly, much less solve them. In many cases of this sort, the partial information given by dimensional analysis may be combined with measurement on only a part of the totality of physical systems covered by the analysis, so that together all the information needed is obtained with much less trouble and expense than would otherwise be possible," p. 81.

"The methods of dimensional analysis are worthy of playing a much more important part as a tool in theoretical investigation than has hitherto been realized. No investigator should allow himself to proceed to the detailed solution of a problem until he has made a dimensional analysis of the nature of the solution which will be obtained, and convinced himself by appeal to experiment that the points of view embodied in the underlying equations are sound," p. 88.

Wilder D. Bancroft

Atoms. *By Jean Perrin. Translated By D. Ll. Hammick. Second English edition. 22×15 cm; pp. xvi+231. New York: D. Van Nostrand Co., 1923. Price: $2.50.* The second English edition is based on the revised form of the eleventh French edition. The first French edition was reviewed eleven years ago (**17**, 563) and the first German one ten years ago (**18**, 451). In this edition the chapters are entitled: chemistry and the atomic theory, molecular agitation; the Brownian movement—emulsions; the laws of the Brownian movement; fluctuations; light and quanta; the atom of electricity; the genesis and destruction of atoms.

"At very low temperatures peculiarities, at first sight hard to explain, are observed with gases as well as with solids. Even at the temperature of melting ice (273° absolute) the specific heat of hydrogen is only 4.75, and is thus distinctly lower than the theoretical value 4.97. The discrepancy is not great, but, as Nernst has justly pointed out, it lies in the direction absolutely irreconcilable with Boltzmann's results on rotational energy. Under his direction investigations have been carried out by Eucken at a very low temperature, and have led to the surprising result that, below 50° absolute, the specific heat of hydrogen becomes 3, as with the monatomic gases! For other gases the specific heat at low temperatures also falls below the theoretical value (though at much lower temperatures than hydrogen), and in fact it seems probable that at sufficiently low temperatures all gases have the same specific heat as the monatomic gases, namely 3; that is to say, the molecules, although not spherical, no longer by their impacts impart to each other rotational energy comparable with their energy of translation," p. 73.

"In short, each molecule of the air we breathe is moving with the velocity of a rifle bullet; travels in a straight line between two impacts for a distance of nearly one ten-thousandth of a millimetre; is deflected from its course 5,000,000,000 times per second, and would be able, if stopped, to raise a particle of dust just visible under the microscope by its own height. There are thirty milliard milliard molecules in a cubic centimetre of air, under normal conditions. Three thousand million of them placed side by side in a straight line would be required to make up one millimetre. Twenty thousand million must be gathered together to make up one thousand millionth of a milligramme," p. 82.

"The objective reality of the molecules becomes hard to deny. At the same time, molecular movement has not been made visible. The Brownian movement is a faithful reflection of it, or, better, it is a molecular movement in itself, in the same sense that the infra-red is still light. From the point of view of agitation, there is no distinction between nitrogen molecules and the visible molecules realised in the grain of an emulsion, which have a gramme molecule of the order of 100000 tons. Of course such grains are not chemical molecules, in which all the cohesive forces are of the nature of those uniting the carbon to the four hydrogen atoms in methane", p. 105.

"If we could examine a solid body with a microscope magnifying 3×10^{10} times the body would appear to us to be composed of extremely dense granules about two millimeters in diameter with a mean distance of about twenty meters between them. . . Matter is porous and discontinuous to an extent far beyond our expectation," p. 161.

"In this connection I should like to add a remark with reference to the *strength of the valency bond*. When at about 2000°C, the dumb-bell-like hydrogen molecule is spinning without rupture perpendicularly to its axis with a frequency but little less than a hundred thousand milliards of revolutions per second, it is obvious that the bond or union between the atoms must be resisting the centrifugal force. A union that would give the same strength to a dumb-bell would have a tenacity at least 1,000 times that of steel," p. 163.

"It seems to me that, for any given molecule, the probable value for the time that must elapse before, under the sole influence of impacts, a certain *fragile* condition will be reached must be smaller the more often the molecule receives impacts per second. Further, supposing this fragile state to have been reached, the probable value for the time required for a molecule to receive the kind of impact capable of rupturing it must again be shorter the more frequent the impacts. For this double reason, if rupture is to be produced by molecular impact, it should occur more frequently (and dissociation should therefore become more rapid) as the concentration of the gas increases.

"Since this is not the case, dissociation cannot be caused by impact. Molecules do not decompose by striking against each other, and we may say: *The probability that any molecule will be ruptured does not depend upon the number of impacts it receives.*

"Since, however, the rate of dissociation depends largely on the temperature, we are reminded that temperature exerts its influence by radiation as well as through molecular impact, and are faced with the suggestion that the cause of dissociation lies in the visible and invisible *light* that fills, under stationary conditions, the isothermal enclosure wherein the molecules of the gases under considerations are moving. *The essential mechanism of all chemical reaction is therefore to be sought in the action of light upon atoms*," p. 164.

Wilder D. Bancroft

The Fundamental Processes of Dye Chemistry. *By H. E. Fierz-David. Translated by F. A. Mason. 24×16cm; pp. xiv+240. New York: D. Van Nostrand Company, 1921. Price: $6.00.*

"The manufacture of synthetic colours has attained to such importance that it seems desirable to familiarise the rising generation of chemical technologists with the methods of production of the more important intermediates. With this end in view, I have attempted a description of these methods in a manner which may be helpful even to those unfamiliar with technical operations.

"Azo colours form the largest section of artificial dyes, and in consequence most attention has been devoted to the preparation of the necessary intermediates. As, however, many of these intermediates are also used in the synthesis of other classes of dyes, such as Indigo, Azines, Thiazines, Aniline Black, Sulphur colours, and Triphenyl-methane dyes, it may fairly be claimed that the field of synthetic colours in its essential features is covered by the present volume.

"To complete the picture I have added recipes for a few dyes and included some general observations on the technique of dye manufacture. With only trifling exceptions the dyes dealt with can all be obtained from the intermediates described in the first portion, so that the student is enabled to obtain a clear view of the stages of development of a dye."

"It has further been found that the manufacture of the intermediate products is far more difficult than that of the finished colouring matters, and, in addition, the apparatus, and machinery needed for the intermediates occupies a far greater space than that required for the actual dyes. The Anthraquinone dyes, however, form an exception to this generalization. With the exception of this last case it may be said that the ratio of the size of the installations and the number of workmen required for intermediates and dyes respectively is approximately as 3:1, or, in other words, a colour factory which has previously purchased its intermediates and now intends to make them itself must enlarge itself about fourfold."

The chapters are entitled: sulphonations; nitrations and reductions; chlorinations; oxidations; condensations; azo dyes; triphenylmethane dyes; sulphur melts; miscellaneous dyes; summary of the most important methods; vacuum distillations in the laboratory and in the works; notes upon the construction and use of autoclaves; structural materials used in dye chemistry; technical notes on works management; example of costing of a simple dye; analytical details.

In several places, pp. 17, 55, 57, stress is laid upon the importance of etching the iron before starting reduction with iron and acetic acid. One wonders whether this is an indirect way of getting a little ferrous salt into solution. The layman is startled to read, p. 55, that "dinitrobenzene is an extremely poisonous substance and quite as dangerous as prussic acid. The workmen who deal with it must always change their clothes and wear gas masks. The substance can even penetrate through the skin into the blood and causes acute cyanosis, a form of poisoning in which the lips of the patient become blue, the pulse weakens, and frequently death supervenes after long illness."

"On the works scale the introduction of chlorine and bromine into aromatic hydrocarbons is carried out almost exclusively by direct halogenation. . . . Benzene readily takes up chlorine in the presence of carriers; iron is the only catalyst of practical importance. In this case the best iron for the purpose is not cast iron but wrought iron, as it acts less vigorously," p. 83.

"Recently attempts have been made to facilitate the introduction of chlorine into the side chain by the use of ultra-violet rays from a Uviol lamp. This only succeeds, however, when there is no trace of iron in the reaction mixture. Even the minute traces of iron in the quartz lamp, or in the porcelain vessels, or the dust of the factory containing iron rust, may cause serious disturbances," p. 93.

Wilder D. Bancroft

L'évolution universelle. *By Branislav Petronievics. 21×13 cm; pp. viii+212. Paris; Félix Alcan, 1921. Price: 7.50 francs.* In the preface the author says that "although written by a metaphysicist, this book is intended as much for the ordinary readers and the scientific men as for the metaphysicist. The ordinary reader will find a clear statement of the chief facts of universal evolution; the scientific man will find a careful discussion of the truth of these facts; while the metaphysicist will find a severe criticism of this discussion."

The subject is presented under three heads: the general bases of evolution; inorganic evolution; organic evolution. In the last chapter on the laws of organic evolution there are given nearly sixty laws, which seems a liberal allowance.

The author considers that there are four main hypotheses in regard to the origin of the world and all that in it is. "The first is the hypothesis of the eternity of things, according to which the inorganic world is eternal and the organic species are eternal and immutable. The metaphysical systems of Aristotle and Spinoza are typical representatives of this hypothesis. The second is the hypothesis of creation according to which the inorganic world and all living forms were created by God; but, once created, have remained immutable. This is the orthodox hypothesis of the Church, and the naturalists Cuvier and Agassiz are the best known upholders of this view. The third hypothesis is that of generalized spontaneous generation, according to which the inorganic world is the product of the transformation of pure thought and living forms are the product of an immediate transformation of inorganic matter. The doctrine of Buddha is the only representative of this hypothesis for the inorganic world while many Greek philosophers—Anaximander, Empedocles, Epicurus—teach the spontaneous generation of all living forms regardless of their complexity. The fourth hypothesis is that of evolution, according to which the inorganic world as it now exists has developed from an original state quite different from the present one, while the living forms have arisen through the transformation of lower into higher forms. Among the scientific men Laplace is the best known protagonist of evolution in the inorganic world; while Lamarck and Darwin occupy a similar position with reference to organic evolution. Among the philosophers the outstanding figures are Kant for the inorganic world and Spencer, Hartmann, and Bergson for the organic world.

Wilder D. Bancroft

Van Nostrand's Chemical Annual for 1922. *Edited by J. C. Olsen. Fifth edition. 19×13 cm; pp. xxii+900. New York: D. Van Nostrand Company. 1922. Price: $4.00.* "In the preface to the fifth edition the editor says: "In the preparation of the Fifth Issue of the Chemical Annual the attempt has been made to maintain the same degree of accuracy as has characterized the former editions. For this purpose a thorough search of the literature has been made for new data on the compounds listed in the Annual, the most reliable constants only having been accepted. A considerable number of compounds have been added to the table of inorganic and organic compounds, particularly the latter. The recent expansion of the manufacture of organic compounds has added to our knowledge of some of these substances, particularly the dye intermediates. Many of these compounds in which chemists are interested could not be included because their constants had not been determined or published. Molecular and atomic weights have been recalculated in accordance with the latest table of atomic weights.

"A careful search was also made for new and useful tables to be added to the list already published. About 46 new tables have been found which are believed to be reliable and of general interest and have been included in this issue. These include a number of tables of ionization of acids and bases, a number of tables giving very complete lists of the chemical and physical properties of some of the chemical elements, a number of new specific gravity and solubility tables as well as some new vapor tension tables."

Wilder D. Bancroft

Explosivstoffe. *By H. Brunswig. Second revised edition. 25×16 cm; pp. xiv+215. Leipzig: Johann Barth, 1923.* The first part deals with the general behavior and the second part with the special behavior of explosives. The chapters are entitled: conditions on which explosions depend; rate of explosions; explosion pressure; explosion temperature; explosion flame; explosion shock; changes of state of explosives; detonators; propellants; blasting explosives; use and treatment of explosives.

An explosion necessitates a sudden increase of pressure which means that at least one of the reaction products shall be a gas or a vapor. Since a high reaction velocity is necessary, an exothermal reaction is more likely to speed up sufficielnty than an endothermal one; but this is not essential. Ammonium nitrate absorbs a large amount of heat; but the change in volume is enormous. The reaction of oxyhydrogen gas to form water means a decrease in volume at constant temperature; but the heat of reaction is sufficient to make the mixture an explosive one.

There is no close relation between the heat of reaction and sensitivity because acetylene is not tremendously sensitive and ammonium hydronitride is; but, in many cases, sensitiveness increases with the heat of reaction. Adsorption of liquids like water, methyl alcohol, acetone, glycerol, vaseline, and the fatty oils decreases sensitiveness very much, p. 12. As is to be expected, a rise of temperature increases the sensitiveness and the effect of friction is to be attributed chiefly to the heat generated thereby, p. 21. Wöhler attributes the specific action of detonators chiefly to the high pressures produced, p. 23.

The effect of a heated wire in igniting explosive mixtures of fire damp is complicated by catalytic action, a copper wire being less effective than a platinum one and more effective than an iron one, p. 41. No experiments seem to have been made on any poisoning action by carbon monoxide. The explosion flame, p. 109, may be composed of a primary flame due to the explosion and a secondary one due to the burning of combustion material scattered by the explosion. Black powder gives a long primary flame and ammonium nitrate a short one. Picric acid gives a short primary flame and a large secondary one. By adding salt to picric acid the secondary flame can be eliminated, though there is an increase in the primary flame, p. 113. For mines where there is much fire damp, only those explosives should be used which give a short primary and no secondary flame.

There is an interesting account, p. 143, of the development of black powder, which the author considers as an outgrowth from Greek fire through the fireworks stage. For six hundred years black powder was the only propellant and the gelatinized, smokeless powders do not run back fifty years. In 1882 Reid and Johnson made a partially gelatinized nitrocellulose powder for sporting purposes and in 1884 von Duttenhofer made the first gelatinized powder for military uses, p. 145. It is claimed that lightning will only set the gelatinized powders on fire and will not cause them to explode, p. 148.

Nitrogelatine consists of nitroglycerine converted into a solid jelly by the addition of small amounts of a special colloid wool which is peptized by nitroglycerine, though the word peptization does not occur in the book and the author evidently believes that in most cases we are dealing with true solutions at some stage.

Cheddite consists usually, p. 183, of 79% potassium chlorate, 1% nitronaphthalene, 15% dinitrotoluene, and 5% castor oil. The nitrocompounds are first dissolved in the oil by warming and the finely powdered chlorate is mixed intimately with the still warm solution. Permonite is a mixture of potassium perchlorate, ammonium nitrate, sodium nitrate, trinitrotoluene, flour and sawdust, gelatinized with glue and glycerine.

A good explosive is obtained when liquid air, enriched to ninety percent oxygen, is taken up by cork charcoal and some petroleum paraffin, or naphthalene is added, p. 187. "Fresh liquid-air cartridges are characterized by a power of action second to none. This high explosive power does not last long and after fifteen to thirty minutes the liquid air evaporates from the cartridge and then there is no explosive left."

When breaking ice in the Rhone river, it was not sufficient to cut grooves in the ice a meter long and 4.5 cm. deep and to fill those with dynamite. The explosion gave rise to long cracks but did not shatter the ice, p. 189. "Vertical holes, 8-10 cm in diameter, were bored in the ice and dynamite cartridges containing 17-30 grams of explosive were stuck through the holes to points about 70 cm below the surface of the ice. Working in this way it was easily possible to shatter a surface of fifty thousand square meters of ice per day."

The beneficial effect of legislative restrictions in regard to storage and handling of explosives is seen clearly in England where the percentage of workmen injured dropped in twenty years from four to one although the number of workmen rose from two thousand to six thousand, p. 190.

Wilder D. Bancroft

THE SUPERSATURATION OF GASES IN WATER AND CERTAIN ORGANIC LIQUIDS[1]

BY JOHN METSCHL[2]

All previous work regarding the supersaturation of gases in liquids may be summarized in a few references. The earliest experiments concerning the evolution of gas bubbles were probably made by Oersted.[3] Later C. F. Schoenbein[4] published an accurate account concerning the supersaturation of gases in aqueous solutions and advanced some rational explanations as to the cause of the evolution of gas bubbles. The term "supersaturated" as applied to gases in water was no doubt first used by D. Gernez[5].

The action of solid bodies upon supersaturated gaseous solutions was investigated in a qualitative way by Charles Tomlinson,[6] F. C. Henrici[7] and H. Schröder.[8] The latter also observed that a sharp and sudden blow upon the walls of the vessel containing the supersaturated solution was apt to cause an evolution of gas due to the momentary decrease of pressure. According to V. Rothmund,[9] Cagniard-Latour[10] had at an earlier date found the same to be true, and in addition noted that vibratory sounds caused the formation of bubbles of gas in supersaturated solutions.

Very little has been done in a quantitative way in respect to gaseous supersaturation. Practically the only investigations in this field were made in recent years by A. Findlay[11] and his co-workers who studied the rate of evolution of carbon dioxide from supersaturated solutions under the influence of colloids and suspensions.

The object of the present investigation was (1) to construct an apparatus by means of which various gases could be dissolved in water and organic liquids under pressures ranging from one to five atmospheres, (2) to saturate these liquids with gas at a pressure higher than one atmosphere, then reduce

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[1] Contribution from the Laboratories of General Chemistry of the University of Wisconsin.

[2] The work included in this paper is from the thesis presented by John Metschl in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. The subject of this research was suggested by Professor James H. Walton and the investigation was conducted under his direction.

[3] Oersted: Gehlen's J. Chem. und Physik, 1, 27 (1806).

[4] Schoenbein: Pogg. Ann., 40, 382 (1837).

[5] Gernez: Compt. rend., 68, 883 (1866).

[6] Charles Tomlinson: Phil. Mag., [4] 34, 136, 229 (1867); 45, 276 (1873).

[7] F. C. Henrici: Pogg. Ann., 147, 555 (1872).

[8] H. Schröder: Pogg. Ann., 137, 76 (1869); Ergänzungsband 5, 87 (1871).

[9] V. Rothmund: "Löslichkeit und Löslichkeitsbeeinflussung," 13 (1907).

[10] Cagniard-Latour: Ann. chim. phys., (11) 56, 252 (1834).

[11] A. Findlay and G. King: J. Chem. Soc., 103, 1170 (1913); 105, 1297 (1914); A. Findlay and O. R. Howell: J. Chem. Soc., 121, 1046 (1922).

the gas above them to atmospheric pressure and by shaking out and measuring the volume of the gas which remained in the liquids in a supersaturated condition, determine the amount of supersaturation for the various pressures.

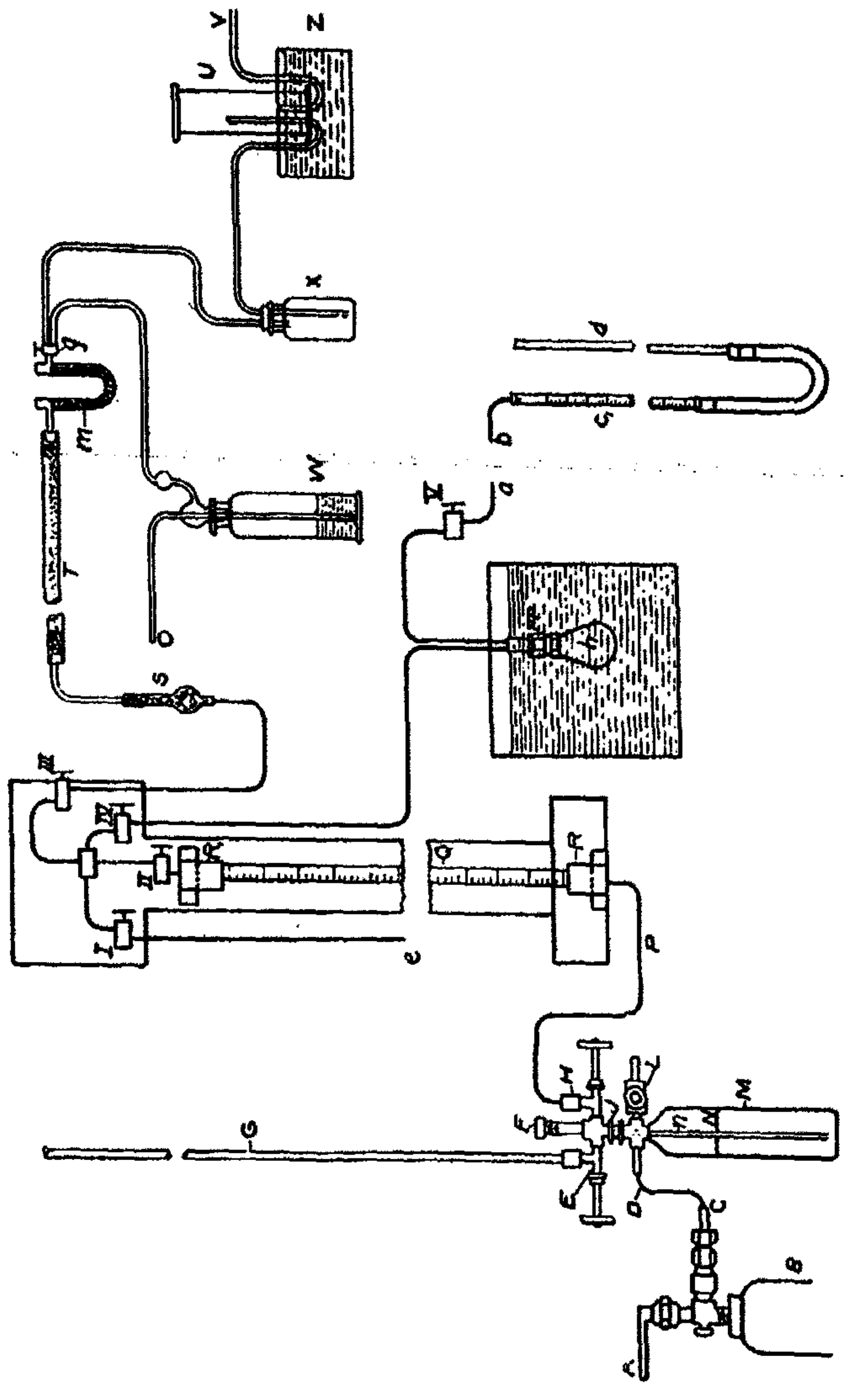

Fig. 1
Pressure Apparatus and Connections

Apparatus

The apparatus shown in Fig. 1 was designed for the purpose of saturating the liquids at various pressures. This apparatus was rendered gas tight only after several months of experimentation. Each valve and connection is an individual problem in itself, consequently the apparatus is described in detail.

M is a steel cylinder which formerly had been an oxygen tank such as is used by dentists in connection with the adminstration of nitrous oxide. The original valve on the tank was removed and replaced by the connections and valves shown in the drawing. These will presently be described. Into the cylinder 900 cc. of purified mercury was placed, the total volume of the tank being about 1400 cc.

L is a Crane, quick-opening, high-pressure steam valve having a bronze body and stem, the latter being fitted with a fiber seat.

n is an iron tube of about 5 mm. diameter which passes through the mercury at *N* and comes within 5 mm. of the bottom of the steel flask *M*. This tube ends at its upper part in the iron bushing *J*, where it communicates with the valves *E* and *H* by means of an iron "T".

The valves *E* and *H* are remodeled, high-pressure steam valves having cast steel bodies and mild steel stems fitting into cast iron seats. One of these valves is shown in section in Fig. 2.

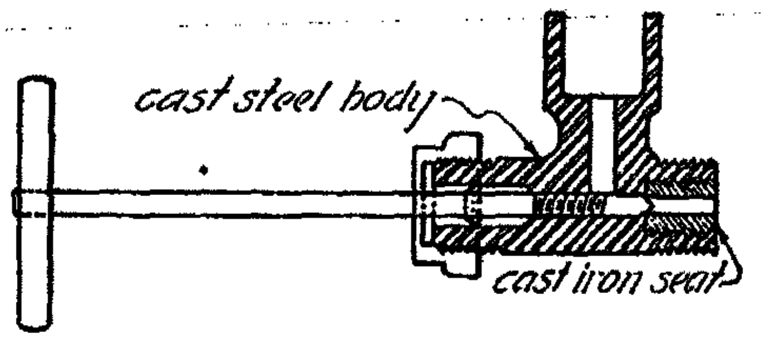

Fig. 2
Tube Valve Scale 4/10

F is an iron cap screwed upon a pipe of the same metal.

G is an open manometer composed of sections of barometer tubing. At its lower end the manometer is held in place in the cup of the valve *E* by means of marine glue.[1] The total height of the manometer was about 10 meters. The mercury column was read by means of meter sticks fastened along side the barometer tubing; the tubing and sticks all being mounted upon a board which extended the entire length of the manometer.

CD is semi-flexible, seamless, copper tubing having an internal diameter of about 1.5 mm. It serves to connect the cylinder *M* with the carbon dioxide tank *B*.

P is an S-shaped tube of steel such as is used in liquid air apparatus. Its internal diameter is 2.5 mm. It is attached to the inside of the cup of the valve *H* by means of marine glue and to the iron cylinder *R* by means of a threaded end.

Q is a graduated Pyrex combustion tube 102 cm. in length with walls 3 mm. thick and a bore of 13 mm. The tube was held in place in the cylinders *R* and R_1 by means of marine glue. A condensing jacket, not shown in the drawing, surrounded the tube. Water from a thermostat was circulated through this jacket by means of a centrifugal pump so that the temperature of the tube was the same as that of the pressure flask *h*.

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[1] The "marine glue" used in this investigation was of the kind employed for waterproofing the canvas in canoe bottoms.

I, *II*, *III*, *IV* and *V* are needle valves, the "needle" or stems of which were tapered and which fitted into conical seats. Their construction is shown in detail in Fig. 3. As mercury was apt to come in contact with valve *II* the latter had all parts made of steel. Valve *V* was subjected to the action of liquids and gases; to eliminate corrosion it had a monel stem and a brass body. The rest of the valves had brass bodies and steel stems.

The tubing between R_1 and valve *II* was also steel, while the connections between the rest of the valves were of seamless copper tubing having an internal diameter of about 1.5 mm.

The whole system of valves, together with the tube *Q* and the cups *R* and R_1 was screwed to a wooden support as shown.

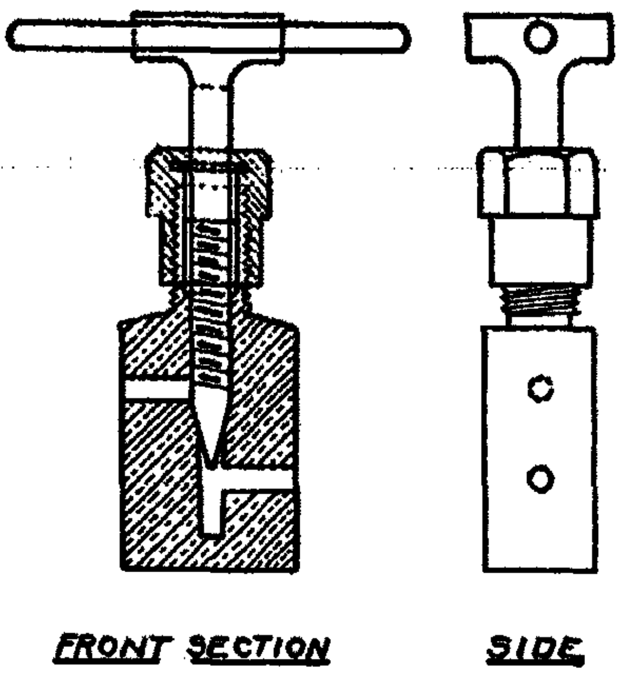

Fig. 3
Needle Valve Scale 4/7

Connection between valve *IV* and the socket *PP* was made by means of semi-flexible brass tubing having an internal diameter of 2 mm. The tubing was bent in the form of a spiral and had a total length of about 1.5 meters. Tubing in this form and of this length readily permitted the pressure flask *h* to be shaken in a horizontal position by means of a suitable shaking device.

Liquids to be supersaturated were placed in the flask *h* which had a capacity of approximately 140 cc., and which was made of well annealed glass with a very smooth internal surface. Flasks of this kind may be obtained from dealers in scientific apparatus in whose catalogues they are described as "pressure flasks."

The flasks used in these experiments had a threaded brass cap fitted to the neck, the cap being held to the glass by means of a low-melting alloy the composition of which is given[1] in George H. Woollatt's "Laboratory Arts."

The alloy is made by melting together:

Bi................	40 parts
Pb................	20 "
Sn................	10 "
Cd................	10 "
Hg................	15 "

Fig. 4 shows the manner in which the brass cap was attached to the neck of the pressure flask, while Fig. 5 shows the flask screwed into its socket.

T is a glass drying tube about a meter in length containing P_2O_5 and loose glass wool.

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[1] "A Teacher's Handbook," 139 (1918).

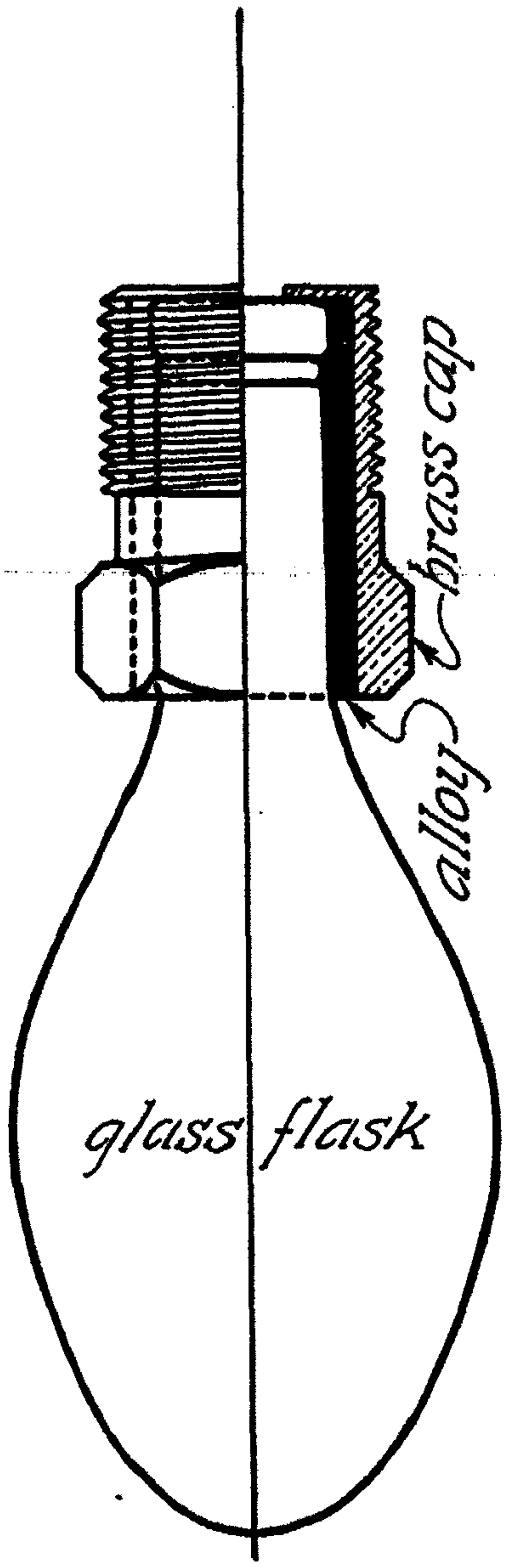

Fig. 4
Pressure Flask with Cap
Scale 5/6

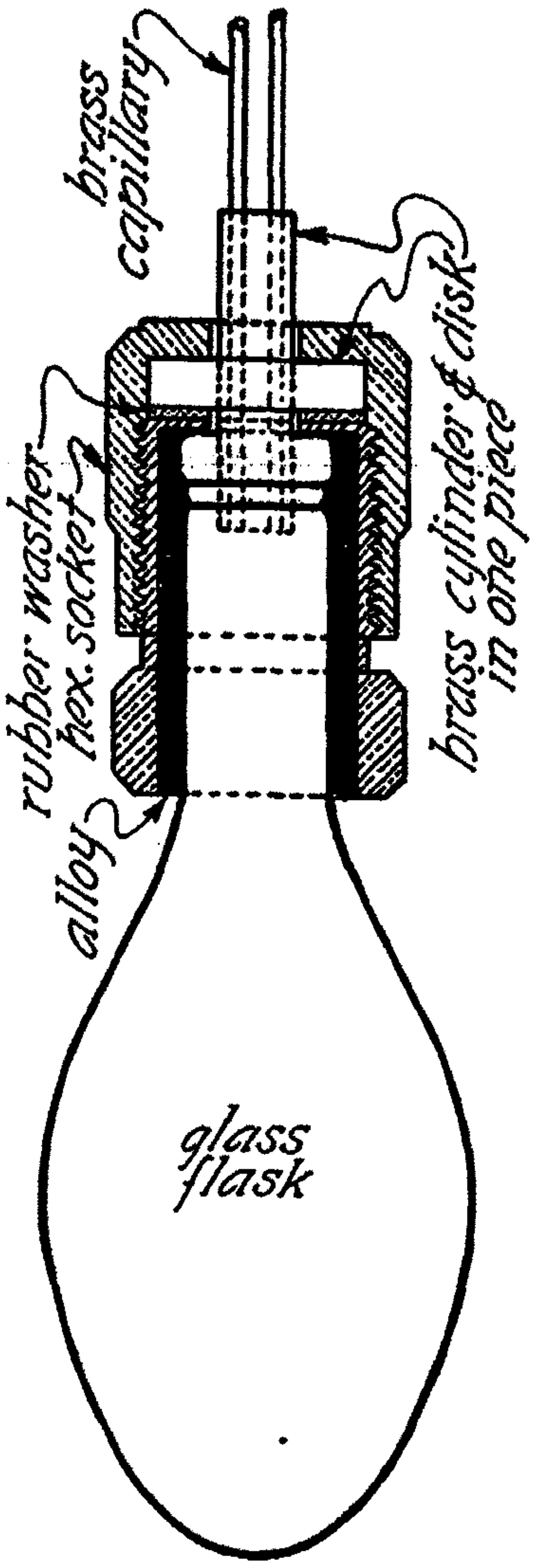

Fig. 5
Pressure Flask with Socket
Scale 2/3

S is a glass tube containing glass wool, its purpose being to remove the particles of P_2O_5 which might be carried along by the gas as it passes through *T'*.

m is a U-tube filled with small lumps of pumice-stone saturated with concentrated sulphuric acid. The purpose of this tube was to remove the greater part of the water from the gas before the latter entered the tube containing the phosphorous pentoxide.

g is a two-way stop-cock.

W is a wash bottle containing concentrated sulphuric acid.

X is a trap to prevent large amounts of water from entering the drying apparatus from the pneumatic trough *Z*.

C_1 is a burette used to measure the volume of gas shaken out of the supersaturated liquids.

d is a leveling tube. The burette and leveling tube contained mercury over which the gas was collected.

The source of the gas used was attached at *V*.

All metal joints from which gas was apt to leak were soldered, while unions of glass to glass, and glass to metal were made tight by the use of marine glue.

Determination of Supersaturation

In making a supersaturation determination the procedure was as follows:

The valves *L, III, IV,* and *V* were closed, while *E, H, I* and *II* were open. The valve upon the carbon dioxide cylinder *B* was then slightly opened by turning the handle *A*. Carbon dioxide now entered the cylinder *M* through *D*. The pressure of the carbon dioxide above the surface of the mercury *N* caused some of the latter to ascend the iron tube *n* and enter the iron "T" where the column of mercury divided, one portion ascending the open manometer *G*, while the other portion entered the pressure tube *Q* through the iron tube *P*.

As soon as the mercury had filled about 5 cm. of the tube *Q* the pressure from the carbon dioxide tank was shut off by closing the valve *A*. Since the manometer *G*, and the tube *e* were open to the atmosphere the levels of the mercury in *G* and *Q* were the same.

When the levels of the mercury in the tubes *G* and *Q* had become equal, the valve *H* was closed. A "Hyvac" oil-pump was now attached to *e* and the space above the mercury in *Q* exhausted. The evacuation usually was carried on for about half an hour. During the evacuation the valve *III* was frequently opened and closed so as to admit some of the gas from the gas jar *U* into the system, the object being to sweep out any foreign gas from the tubes and valves.

To be reasonably certain of removing foreign gas from the tubes and valves it was customary to pass some of the gas to be experimented with, through the system by attaching the gas generator at *O* and passing gas through for about an hour before the tube *Q* was evacuated. This procedure was, however, only resorted to when the gases were changed during the course of the investigation.

The next step was to close valve *I* and transfer the connection of the oil pump from *e* to *a*. The pressure flask *h* containing the desired liquid was then screwed into its socket *PP*. The attached flask was now placed into a can of hot water, and the oil pump started, the valve *V* being open, but *IV* being closed as before. The purpose of this part of the procedure was to boil the liquid in the flask *h* under reduced pressure so as to remove gases dissolved in it. After ebullition had gone on in this manner for ten to fifteen minutes, the valve *V* was closed and the connection of the oil pump detached from *a*. The pressure flask was then placed into the horizontal shaking device in the thermostat and its contents allowed to assume the temperature of the bath which was 25°C. in all cases.

Valve *II* was next closed, and valves *IV* and *III* opened, valves *I* and *V* being closed as before. Gas now entered from *U* into the pressure flask *H* which was shaken in order to saturate the liquid contained therein at atmospheric pressure. As the gas entered the pressure flask the water rose in the gas jar *U*. In order that the liquid in the pressure flask be saturated with the gas at atmospheric pressure the water levels in *U* and *Z* were kept the same during the absorption process.

After the absorption of gas by the liquid contained in *h* had ceased, valves *II* and *H* were opened. The gas in the whole system was now under the prevailing atmospheric pressure, and the mercury levels in *G* and *Q* were the same. These levels were recorded as was also the barometric pressure. After this valve *III* was closed.

All was now in readiness for the saturation of the liquid in *h* under pressure. This was accomplished by slightly opening the valve *A* on the carbon dioxide cylinder *B*, whereupon the mercury in *G* and *Q* began to ascend. As the mercury rose in *Q* it compressed the gas above it and forced some of it into the liquid contained in the pressure flask. Throughout this procedure the pressure flask was vigorously shaken in the thermostat, and water from the latter was caused to flow through the glass jacket surrounding the pressure tube *Q*.

When the desired pressure had been attained, the valve *A* was closed and the shaking of the flask continued until there was no further change in the mercury levels in the tubes *G* and *Q*. These levels were then recorded. Obviously the difference in level between *G* and *Q* gave the pressure upon the surface of the liquid in *h*. The absolute pressure in *h* was obtained by adding the barometric pressure to the above difference in level.

The shaking of the flask was next stopped and the valve *IV* closed. The end of the tube *a* was inserted into a small vessel of water to a depth of about 2 mm. and the valve *V* opened. The gas above the liquid in *h* now escaped. When it ceased to come off, as could be ascertained when no more bubbles were formed in the water from the tube *a*, connection was made by means of a thick-walled, short piece of rubber tubing of small diameter with the tube *b*.

The shaker was again started and the gas which was in the liquid of the flask *h* in a supersaturated condition was shaken out and its volume determined in the burette C_1.

Since the total volume of the flask *h* was known it was easy to find the volume of the liquid which had been previously boiled under reduced pressure and then saturated with gas at the higher pressure.

It was only necessary to fill up the flask from a burette with the same kind of liquid which had been used in the experiment, and subtract the volume added from the total volume of the flask. From this and the foregoing data the amount of supersaturation per unit volume of the liquid could be ascertained.

To make the next supersaturation determination with the same kind of gas was comparatively simple. The valve *L* was opened for a short time so that some of the carbon dioxide in the cylinder *M* escaped. This caused the mercury in the tubes *G* and *Q* to descend and when the valve *III* was opened, gas from *U* was drawn into the system.

By suitable manipulation of the valves a wide range of pressure can be brought to bear upon the liquid in the pressure flask. The only limits to the amount of pressure which can be applied are the strength of the various components of the apparatus and the pressure in the carbon dioxide cylinder itself.

Following is an example of how the data for each determination were recorded:

Method of recording Data

Date. April, 18th, 1923.
Temp. Room. 27°.5 C.
Gas used. Nitrogen.
Liquid used. Ethyl alcohol, 98% by wt.
Vapor press. C_2H_5OH at 27°.5C. } 68 mm.

Total vol. of press. flask (*h*)	139.44 cc. at 25°C.
cc. C_2H_5OH added to flask after experiment	42.20
	97.24 cc. C_2H_5OH used in exp.
Manometer (*G*) read. at end of exp.	1513 mm.
Manometer read at start of exp.	98 mm.
No. of mm. of Hg on Manometer	1415
Tube (*Q*) read. at start of exp.	768 mm.
Tube read. at end of exp.	148 mm.
No. of mm. of Hg on tube	620
No. of mm. of Hg on Manometer	1415
No. of mm. of Hg on Tube	620
No. of mm. of Hg on Liquid	795 = P
Barometric pressure	741 mm.
Absolute press. on Liquid	1536 mm.

Burette (C_1) read. at end of exp.	16.90 cc.
Burette read at start of exp.	0.80
Vol. of gas shaken out	16.10 cc.

Vol. of gas per 100 cc. of $C_2H_5OH = \frac{16.10}{97.24} \times 100 = 16.55$cc. at 768 mm. and 27°.5 C.

Vol. of gas per 100 cc. of C_2H_5OH at 760mm. and 0°C. $= 13.31$cc. $= V$

$V/P = \frac{13.31}{795} = 0.01674.$

The letters h, G, Q and C_1 in the above table refer to the corresponding letters in Fig. 1 with which the apparatus in question is denoted.

Experimental

The Supersaturation of Oxygen in Water

The supersaturation of oxygen in water had previously been observed by A. H. Gill[1] and C. A. Seyler[2].

It was thought of interest to investigate the supersaturation of oxygen in water and other liquids to a greater extent with the apparatus previously described.

The oxygen used was of the kind which can be obtained in a compressed state in steel cylinders. It had been made by the Linde process and was about 97% pure. However, some determinations were made also with oxygen obtained by dropping distilled water upon sodium peroxide. No difference could be observed in the oxygen from these two sources in the course of the determinations.

Conductivity water was used in these experiments.

TABLE I

Supersaturation of Oxygen in Water

Vol. H_2O cc.	Vol. O_2 Shaken out cc.	Vol. O_2/ 100cc. H_2O	t°C.	Vol. O_2 Std. Cond. cc. = V	Press. Man. mm. P	Abs. P′ mm.	V/P
98.23	0.88	0.90	24.5	0.78	224	969	0.00347
94.74	1.25	1.32	25.0	1.14	337	1079	0.00338
97.25	1.90	1.95	24.0	1.69	476	1216	0.00355
98.20	2.70	2.75	25.5	2.38	732	1474	0.00325*
97.80	4.35	4.45	25.0	3.85	1036	1777	0.00372
98.64	5.90	5.98	23.0	5.26	1547	2293	0.00340
97.84	7.95	8.13	23.0	7.14	2088	2833	0.00342*
97.99	10.15	10.35	20.0	9.09	2687	3421	0.00338*
98.12	11.33	11.55	20.0	10.13	2962	3695	0.00342
						Av.	0.00344

*Indicates determinations made with oxygen obtained from sodium peroxide and water.

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[1] A. H. Gill: J. Anal. App. Chem., 6, No. 11.

[2] C. A. Seyler: Chem. News, 67, 87 (1893).

$S_{25} = 2.83$ Winkler, from tables in Landolt-Börnstein.
$S_{25} = 2.90$ Bohr and Bock, from tables in Landolt-Börnstein.
$s_{25} = 2.60$ From supersaturation data.

The figures in the first column of Table I give the volume of water in the pressure flask *h* (see Fig. 1) which was saturated with oxygen at the higher pressure.

The volume of oxygen shaken out of the water in the pressure flask, after the pressure in the latter had been reduced to atmospheric, is given in the second column. Temperatures at which these volumes were measured in the burette C_1 (see Fig. 1) are given in the fourth column.

In the third column is the volume of oxygen shaken out of 100 cc. of water, at the temperature indicated in column four. The values in column three were obtained from those in columns one and two.

The fifth column gives the volumes of column three reduced to standard conditions of temperature and pressure.

Pressures indicated by the manometer *G* (see Fig. 1) are given in the sixth column. These values indicate the pressure at which the liquid in the pressure flask was saturated.

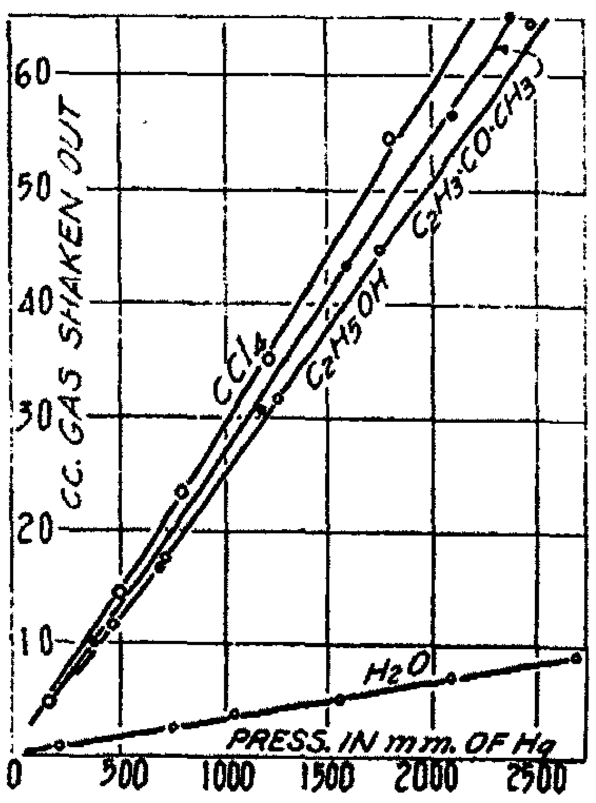

FIG. 6

Supersaturation of Oxygen in Water and Organic Liquids

Column seven gives the absolute pressure at which the liquid in the pressure flask was saturated, that is, these values represent the pressure of the manometer plus the barometric pressure.

The ratio of the values in columns five and six are represented in the eighth column.

The values in columns five and six were plotted to form the oxygen-water graph shown in Fig. 6.

S_{25} represents the volume of gas absorbed in 100 cc. of liquid at 25°C., and 760 mm. according to the given observer. This value represents the Bunsen absorption coefficient multiplied by one hundred.

s_{25} represents the volume of gas shaken out of the supersaturated gaseous solution at 25°C., when the pressure upon the solution had been reduced from 760 mm. to atmospheric pressure. The value for s_{25} was obtained by plotting the data of columns five and six upon larger sized co-ordinate paper than shown in Fig. 6, and reading off the volume of gas shaken out which corresponded to a pressure of 760 mm. It must, however, be remembered that the value s_{25} gives the volume of gas shaken out when the *absolute* pressure above the solution really amounted to two atmospheres, but when the pressure was reduced to one half of this amount the volume indicated by s_{25} could be shaken out, while the gas dissolved at one atmosphere remained in solution.

The graph in Fig. 6 shows that the volume of oxygen shaken out of 100 cc. of water—or the supersaturation— is approximately proportional to the pressure at which the water was saturated.

With greater refinements of measurements and more careful methods of manipulation it is probably that the above supersaturation measurements could be used for determining the solubility of some gases in liquids at higher pressures.

Supersaturated solutions of oxygen in water appear to possess considerable stability. When the experiments in this connection were first begun it was thought that the pressure above the water had to be released very gradually so as not to disturb the metastable solution below. Consequently the gas was released so that all above the solution came off in 15-20 minutes. This method was inconvenient and consumed a good deal of time. Determinations were then made in which the valve upon the pressure flask was opened wide so that all of the gas escaped in a few seconds. No apparent differences in the final results could be detected when the supersaturated solution was shaken to measure the volume of oxygen given off. Only at the higher pressures indicated in Table I, in some cases could a few bubbles be observed rising out of the water when the pressure was suddenly released. But this was the exception rather than the rule. Effervescence was in no instance observed. Neither did the gas appear to come off spontaneously from the water after the pressure above it had been released.

This could be shown in the following manner: When the desired pressure in the flask had been obtained, the connection from valve *V* (Fig. 1) was inserted for a distance of about 2 mm. in water previously saturated with oxygen. Then valve *V* was quickly opened to its fullest extent allowing the gas above the water in the flask to come out with a rush. A period of quiet ensued. No bubbles formed at the end of the connection in the water indicating that very little, if any gas, was coming from the surface of the supersaturated solution. Even after an interval of 5-10 minutes no bubble formation could be noticed. To borrow a phrase used by Findlay[1] supersaturated solutions of oxygen in water probably have a considerable "period of quiescence". No doubt, if the pressure had been increased sufficiently the period of quiescence could have been reduced, but it was not convenient to investigate this farther at the time.

The relative stability of the supersaturated oxygen in water solution could be shown in a still more striking way. The pressure flask containing the metastable solution could be unscrewed from its socket without exercising extraordinary care with regard to the sensitiveness of the solution. The bottom of the flask could be bumped against the table, or the sides could be rapped with a block of wood but as long as the surface of the liquid remained

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[1] Findlay: loc. cit

unbroken no bubbles of gas could be seen to be evolved out of the solution. Only upon shaking the flask so as to break the surface of the liquid could numerous fine bubbles of gas be caused to rise out of the solution, but as soon as the shaking stopped the bubble formation also soon ceased. The shaking had to be continuous and prolonged if all the supersaturated gas was to be obtained from the water. The length of time during which the oxygen remained in contact with the water while under pressure apparently did not influence the results. In the earlier experiments all solutions were kept in contact with the oxygen for fifteen minutes before the pressure was released. Later the same results were obtained when the solution was shaken as soon as the manometer showed that equilibrium was established, which was two minutes at the most. Neither were any differences detected after the solution was allowed to stand in contact with the gas for an hour.

The Supersaturation of Oxygen in Carbon Tetrachloride

As far as could be ascertained no experiments have been made using organic liquids as solvents in the study of gaseous supersaturation. Accordingly this phase of the problem was investigated to a limited extent.

The carbon tetrachloride used was obtained from L. B. Parsons of this laboratory who employed the same kind in his study of the reactions between dry reagents. It was of the C. P. variety and had been allowed to stand three months in contact with sticks of potassium hydroxide before distillation. The oxygen used was of the kind which is sold compressed in steel cylinders.

TABLE II

Supersaturation of Oxygen in Carbon Tetrachloride

Vol. CCl_4 cc.	Vol. O_2 Shaken out cc.	Vol. O_2/100 cc. CCl_4	t°C.	Vol. O_2 Std. Cond. cc. = V	Press. Man. mm. P	Abs. P′ mm.	V/P
96.44	5.95	6.17	24.5	4.68	168	906	0.0278
98.44	18.60	18.89	24.0	14.39	488	1226	0.0295
95.79	29.50	30.79	24.5	23.34	757	1495	0.0308
96.04	29.70	30.92	26.0	23.36	783	1530	0.0298
94.84	41.00	43.23	24.0	32.93	1160	1898	0.0284
93.54	41.40	44.25	21.0	34.92	1217	1939	0.0287
97.24	44.10	45.35	23.0	35.38	1232	1979	0.0287
95.29	48.80	51.21	23.0	39.95	1375	2122	0.0291
96.64	66.10	68.39	20.0	54.66	1792	2534	0.0305
95.64	96.80	101.20	26.5	74.63	2489	3224	0.0300
						Av.	0.0283

S_{25} = no data available for 25°C.

s_{25} = 22.5 from supersaturation data.

The data from columns five and six were used in plotting the graph shown in Fig. 6.

All values for the corrections for vapor tension which were applied for the reduction of the gas volumes to standard conditions were taken from the tables in Landolt and Börnstein.

Because of the large volume of gas which was shaken out of the carbon tetrachloride at the higher pressures it was impractical to make more determinations at more elevated pressures since the burette in which the gas was measured proved to be too small. By using approximately half the volume of carbon tetrachloride than had been used as shown in the data of column one, the ratio V/P dropped to values ranging between 0.0219 and 0.0258. This seems to indicate that some relation exists between the volume of solvent and the amount of gas it can retain when the system is supersaturated. This phase was not farther investigated.

The Supersaturation of Oxygen in Ethyl Alcohol

The alcohol used had been treated with metallic sodium previous to distillation. It had a specific gravity of 0.7992 at 15°C., which corresponds to about 98% ethyl alcohol by weight. The oxygen was from the same source as in the preceding experiments.

Table III

Supersaturation of Oxygen in Ethyl Alcohol

Vol. Alc. cc.	Vol. O_2 Shaken out cc.	Vol. O_2/100 cc. Alc.	t°C.	Vol. O_2 Std. Cond. cc. = V	Press. Man. mm. P	Abs. P′ mm.	V/P
97.94	13.80	14.09	26.0	11.54	464	1209	0.0249
96.99	20.70	21.34	27.0	17.29	691	1434	0.0256
95.89	37.00	38.58	27.0	31.26	1267	2010	0.0247
95.94	51.00	53.16	27.0	43.08	1644	2387	0.0262
96.84	52.90	54.62	26.0	44.74	1738	2483	0.0257
97.84	77.00	78.73	26.0	64.49	2476	3221	0.0260
95.99	79.10	82.40	26.0	67.99	2654	3404	0.0256
						Av.	0.0255

S_{24} = 19.94 for 99.7% alcohol at 24°C. Timofejew: Z. physik. Chem., 6, 151 (1890).

s_{25} = 19.5 from supersaturation data.

The data in columns five and six were plotted to obtain the alcohol-oxygen graph in Fig. 6.

The Supersaturation of Oxygen in Acetone

The acetone used was of the C. P. variety and stood over anhydrous copper sulphate two weeks before it was distilled. The oxygen was obtained from the same source as in the previous experiments.

TABLE IV

Supersaturation of Oxygen in Acetone

Vol. Acet. cc.	Vol.O_2 Shaken out cc.	Vol.O_2/ 100 cc. Acet.	t°C.	Vol.O_2 Std. Cond. cc. = V	Press. Man. mm. P	Abs. P′ mm.	V/P
88.94	13.80	15.51	22.5	10.38	398	1149	0.0261
94.64	24.90	26.31	24.5	16.86	676	1427	0.0249
94.79	44.80	47.26	23.5	30.85	1164	1914	0.0265
94.62	64.70	68.38	24.0	43.24	1579	2318	0.0274
94.44	87.40	92.54	25.5	56.44	2097	2836	0.0269
92.29	100.00	108.30	26.0	65.30	2364	3102	0.0276
						Av.	0.0266

$S_{25} = 19.48$ Levi: Gazz. chim. ital., **31**, II, 513 (1901).
$s_{25} = 20.0$ From supersaturation data.

It should be mentioned that determinations made at the higher pressures, particularly the one at 2364 mm., that the oxygen came out of the supersaturated solution at an appreciable rate as soon as the pressure upon it was released. At the above mentioned pressure the gas came off at the rate of 4 cc. per minute without shaking the pressure flask.

The Supersaturation of Nitrogen in Water

Nitrogen was obtained by a method used by Just[1] in his solubility determinations. Conductivity water was used as in the case of the experiments with oxygen and water.

TABLE V

Supersaturation of Nitrogen in Water

Vol.H_2O cc.	Vol.N_2 Shaken out cc.	Vol.N_2/ 100 cc. H_2O	t°C.	Vol.N_2 Std. Cond. cc. = V	Press. Man. mm. P	Abs. P′ mm.	V/P
92.64	1.20	1.30	28.0	1.10	584	1325	0.00189
96.74	1.80	1.86	26.5	1.59	899	1639	0.00177
92.64	2.00	2.16	28.0	1.84	914	1655	0.00201
98.54	1.80	1.83	25.0	1.58	921	1662	0.00171
96.74	3.00	3.10	24.0	2.69	1489	2229	0.00181
96.74	4.20	4.34	18.0	3.88	1847	2587	0.00210
97.84	5.10	5.21	25.5	4.65	2153	2895	0.00216
92.61	6.00	6.48	27.0	5.54	2800	3541	0.00198
						Av.	0.00193

$S_{25} = 1.53$ Just: loc. cit.
$S_{25} = 1.50$ Bohr and Bock, from tables in Landolt-Börnstein.
$s_{25} = 1.50$ From supersaturation data.

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[1] Just: Z. physik. Chem., **37**, 342 (1901).

As in the previous experiments the data from the fifth and sixth columns were plotted and the water-nitrogen graph of Fig. 7 was obtained.

The values for V/P are not in as good agreement with each other as might be desired. This may be due to the fact that a different valve was used in place of valve *V* of the former experiments (see Fig. 1). The new valve had a comparatively large cavity about its seat into which water condensed when the water in the pressure flask was boiled under reduced pressure to remove the air. In the shaking out process the water in the cavity apparently interfered with the movement of the gas through the valve, which may partly account for the somewhat erratic results. Moreover, the last portion of the gas in the supersaturated solution came off very slowly, so that prolonged shaking was necessary to obtain a constant reading upon the burette. Thus insufficient shaking might result in a second source of error.

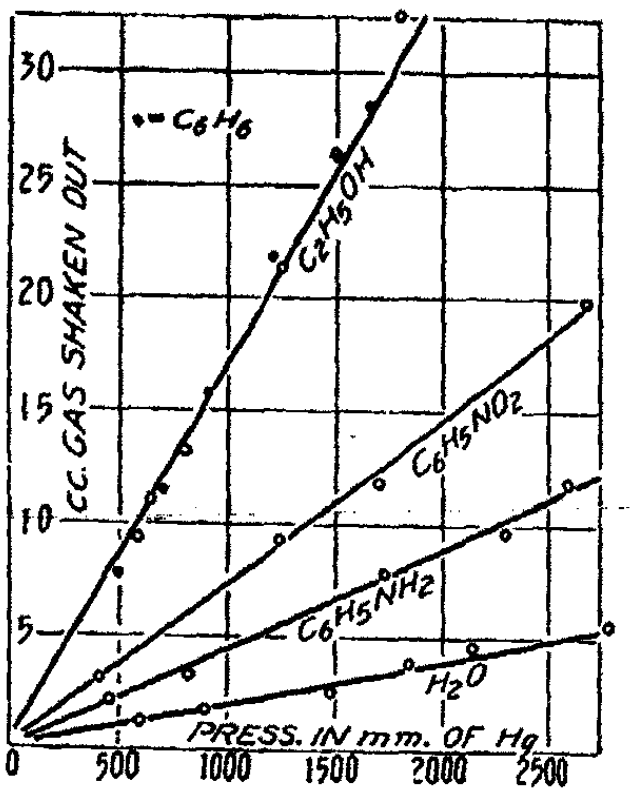

Fig. 7
Supersaturation of Nitrogen in Water and Organic Liquids

The Supersaturation of Nitrogen in Ethyl Alcohol

The alcohol was of the same kind as was used in the supersaturation of oxygen in alcohol. Nitrogen was obtained in the same manner as mentioned in the preceding experiment.

Table VI

Supersaturation of Nitrogen in Ethyl Alcohol

Vol. Alc. cc.	Vol. N_2 Shaken out cc.	Vol. N_2/ 100 cc. Alc.	t°C.	Vol. N_2 Std. Cond. cc. = V	Press. Man. mm. P	Abs. P′ mm.	V/P
97.24	11.40	11.72	28.0	9.38	576	1317	0.0163
96.34	13.30	13.80	28.0	11.03	642	1383	0.0172
97.24	16.10	16.55	27.5	13.31	795	1536	0.0167
97.24	25.20	25.91	25.0	21.29	1247	1988	0.0171
97.24	31.60	32.49	27.0	26.25	1488	2229	0.0176
97.24	39.30	40.41	27.5	32.50	1800	2541	0.0181
96.34	50.20	52.10	28.0	41.65	2385	3126	0.0175
						Av.	0.0172

S_{25} = 13.11 Just: loc. cit.
s_{25} = 13.0 From supersaturation data.

From the data in Table VI the alcohol-nitrogen graph in Fig. 7 was obtained in a similar manner as were the graphs of the preceding experiments.

At the manometric pressure of 1488 mm. and above, the gas came off at a noticeable rate without shaking the pressure flask when the pressure upon the supersaturated solution was released. This is similar to the observation made in connection with the supersaturation of oxygen in acetone, already referred to. The nitrogen came out of the supersaturated solution very readily upon shaking. Constant readings upon the burette were rapidly obtained and the last portion of the gas did not seem to be held as tenaciously by the alcohol as was the case of nitrogen in water.

In this and the experiments following a new portion of liquid was not always put into the pressure flask for each supersaturation determination as long as the same kind of gas was being investigated. The gas in the supersaturated state was merely shaken out, its volume determined, and the same liquid again used for another determination, but saturation being made at a higher pressure. It was not deemed necessary to boil the liquid after each determination to make it gas free as long as it had once been boiled and then saturated with the gas in question. This fact accounts for the similarity in the volumes in the first columns of some of the later tables.

The Supersaturation of Nitrogen in Benzene

Dry benzene was obtained from Dr. L. B. Parsons already mentioned in connection with the supersaturation experiments of oxygen in carbon tetrachloride. Nitrogen was obtained in the manner previously mentioned.

TABLE VII

Supersaturation of Nitrogen in Benzene

Vol. C_6H_6 cc.	Vol. N_2 Shaken out cc.	Vol. N_2/100 cc. C_6H_6	t°C.	Vol. N_2 Std. Cond. cc. = V	Press. Man. mm. P	Abs. P′ mm.	V/P
91.14	8.00	8.78	27.0	7.72	492	1228	0.0157
91.14	11.90	13.05	27.0	11.48	688	1424	0.0167
91.14	16.20	17.77	27.5	15.63	888	1624	0.0176
91.14	22.60	24.79	28.0	21.71	1190	1926	0.0182
91.14	29.90	32.81	28.0	28.73	1659	2395	0.0173
93.59	40.20	42.95	29.0	37.33	2281	3015	0.0164
						Av.	0.0170

S_{25} = 10.61. Just: loc. cit.

s_{25} = 13.0 From supersaturation data.

No reason can be given for the lack of agreement between the solubility and supersaturation measurements as given in the above table. When the pressure on the manometer was 1190 mm. and above the gas came out of the supersaturated solution at an appreciable rate without shaking the flask.

The Supersaturation of Nitrogen in Nitrobenzene

The nitrobenzene employed was of the C. P. variety. It had been allowed to stand over calcium chloride about two weeks previous to distillation. The nitrogen was obtained by the same method as in the preceding experiments.

TABLE VIII

Supersaturation of Nitrogen in Nitrobenzene

Vol. $C_6H_5NO_2$ cc.	Vol. N_2 Shaken out cc.	Vol. N_2/100cc. $C_6H_5NO_2$	t°C.	Vol. N_2 Std. Cond. cc. = V	Press. Man. mm. P	Abs. P′ mm.	V/P
97.74	3.40	3.48	29.5	3.03	416	1149	0.00728
97.74	4.50	4.60	29.5	4.01	549	1282	0.00730
97.74	10.30	10.53	29.5	9.16	1238	1971	0.00740
97.74	13.40	13.71	30.0	11.91	1688	2421	0.00706
97.74	22.30	22.81	30.0	19.88	2707	3440	0.00734
						Av.	0.00728

S_{25} = 5.729. Just: loc. cit.
s_{25} = 5.6 From supersaturation data.

The nitrobenzene-nitrogen graph of Fig. 7 was obtained in a similar manner as were the graphs in the previous determinations. When the pressure upon the supersaturated solution was released no evolution of gas was noticeable even at the highest pressures shown in Table VIII unless the pressure flask was shaken. This is in counterdistinction to the fact observed in the case of nitrogen in benzene.

The Supersaturation of Nitrogen in Aniline

The aniline used had been allowed to stand over sticks of potassium hydroxide for two weeks previous to distillation. The nitrogen was prepared in the same way as in the previous determinations.

TABLE IX

Supersaturation of Nitrogen in Aniline.

Vol. $C_6H_5NH_2$ cc.	Vol. N_2 Shaken out cc.	Vol. N_2/100 cc. $C_6H_5NH_2$	t°C.	Vol. N_2 Std. Cond. cc. = V	Press. Man. mm. P	Abs. P′ mm.	V/P
98.69	2.40	2.43	29.0	2.12	470	1203	0.00451
98.69	3.90	3.95	29.0	3.44	822	1555	0.00419
98.69	7.50	7.60	29.0	6.62	1523	2256	0.00435
98.69	10.70	10.84	25.0	9.60	2344	3079	0.00410
99.87	12.20	12.35	25.0	10.90	2613	3348	0.00419
						Av.	0.00427

S_{25} = 2.815. Just: loc. cit.
s_{25} = 3.3 From supersaturation data.

The aniline-nitrogen graph of Fig. 7 was obtained in a manner similar to the graphs of the preceding experiments. The supersaturated solution of nitrogen in aniline had to be shaken for a considerable length of time because the gas was tenaciously held by the liquid even at the highest pressures shown in Table IX.

The Supersaturation of Air in Water

The air was drawn into the pressure apparatus through a tube extending outside the building. Conductivity water was used as in the cases of oxygen and nitrogen.

Table X

Supersaturation of Air in Water

Vol. H_2O cc.	Vol. Air Shaken out cc.	Vol. Air/ 100cc of H_2O	t°C.	Vol. Air Std. Cond. cc. = V	Press. Man. mm. P	Abs. P′ mm.	V/P
97.54	2.10	2.15	26.0	1.85	880	1622	0.00210
97.54	4.60	4.72	25.5	4.07	1765	2507	0.00231
97.54	5.70	5.84	25.0	5.06	2421	3163	0.00209
98.44	6.80	6.91	25.0	5.98	2730	3472	0.00219
						Av.	0.00212

$S_{25} = 1.724$. Winkler, from tables in Landolt-Börnstein.

$s_{25} = 1.65$ From supersaturation data.

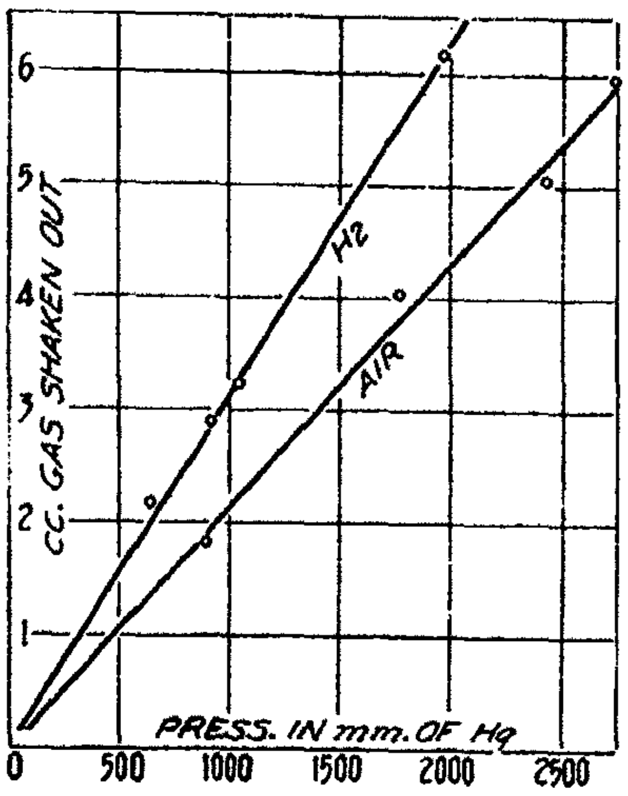

Fig. 8
Supersaturation of Air and Hydrogen in Water

The air-water graph of Fig. 8 was plotted from the data in Table X as had been done in the previous experiments.

The air was tenaciously held by the water and only when the shaking of the supersaturated solution was somewhat prolonged could the last portion be gotten out.

The Supersaturation of Hydrogen in Water

The hydrogen was obtained by the use of aluminum amalgam as described by Just.[1]

Conductivity water was used as in the previous experiment.

Table XI

Supersaturation of Hydrogen in Water

Vol. H_2O cc.	Vol. H_2 Shaken out cc.	Vol. H_2/ 100cc. of H_2O	t°C.	Vol. H_2 Std. Cond. cc. = V	Press. Man. mm. P	Abs. P′ mm.	V/P
91.69	2.30	2.51	22.0	2.18	641	1375	0.00340
91.69	3.00	3.27	21.0	2.87	902	1636	0.00318
91.69	3.40	3.71	22.0	3.25	1052	1786	0.00309
91.69	6.60	7.20	24.5	6.18	1958	2692	0.00316
92.16	7.80	8.46	25.0	7.24	2255	2989	0.00321
						Av.	0.00321

$S_{25} = 1.759$ Winkler, from tables in Landolt-Börnstein.

$S_{25} = 1.822$. Just: loc. cit.

$s_{25} = 2.35$. From supersaturation data.

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[1] Just: loc. cit.

No reason can be assigned for the lack of agreement between the supersaturation and solubility data as shown in Table XI.

The Supersaturation of Carbon Dioxide in Water

That supersaturated solutions of carbon dioxide in water occur has been known for a considerable time. Both Liebig[1] and L. Pratesi[2] had observed the supersaturation of carbon dioxide in mineral water.

The carbon dioxide used in the following experiments was obtained from marble chips and pure hydrochloric acid.

TABLE XII

Supersaturation of Carbon Dioxide in Water

Vol. H_2O cc.	Vol. CO_2 Shaken out cc.	Vol. CO_2/ 100cc. of H_2O	t°C.	Vol. CO_2 Std. Cond. cc. = V	Press. Man. mm. P	Abs. P′ mm.	V/P
94.19	25.0	26.54	25.0	22.77	420	1156	0.0542
96.54	36.8	38.11	27.0	32.43	502	1240	0.0646
94.05	19.9	21.15	25.0	18.32	602	1345	0.0304
96.79	63.0	65.09	24.0	56.74	879	1647	0.0646
96.64	60.4	62.50	24.5	53.79	922	1658	0.0583
94.94	67.8	71.41	26.0	61.15	1125	1863	0.0544
96.54	106.7	110.50	26.0	94.63	1873	2611	0.0505
						Av.	0.0541

$S_{25} = 75.90$. Bohr and Bock, from tables in Landolt-Börnstein.

$S_{25} = 75.62$. Just: loc. cit.

$s_{25} = 40.40$. From supersaturation data.

There is no agreement between the supersaturation result and any of the solubility determinations. The low value from the supersaturation data is probably due to the escape of gas from the supersaturated solution as soon as the pressure upon it is released. Findlay and King[3] found that supersaturated solutions of carbon dioxide in water were exceedingly sensitive to slight mechanical shock. As the gas above the solution in the pressure flask was released with a rush, it is possible that a portion of the carbon dioxide came out of the solution as a result. The same investigators mentioned above surmised that if solutions of carbon dioxide were saturated at a higher pressure that there would be no period of quiescence when the pressure is reduced. This seems to be corroborated in the cases of carbon dioxide in water and ethyl alcohol. Because of the lack of agreement between the solubility measurements and the supersaturation data no graphs are shown for the supersaturation of carbon dioxide in water and ethyl alcohol.

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[1] Liebig: Ann., **30**, 4 (1839).

[2] L. Pratesi: Gazz. chim. ital., **22**, 493 (1892).

[3] Findlay and King: J. Chem. Soc., **103**, 1170 (1913).

The Supersaturation of Carbon Dioxide in Ethyl Alcohol

The same kind of alcohol was used as in the case of the supersaturation of oxygen in ethyl alcohol. The carbon dioxide was obtained by the method already described.

TABLE XIII

Supersaturation of Carbon Dioxide in Ethyl Alcohol

Vol. Alc. cc.	Vol.CO_2 Shaken out cc.	Vol.CO_2/ 100cc. of Alc.	t°C.	Vol.CO_2 Std. Cond. cc. = V	Press. Man. mm. P	Abs. P′ mm.	V/P
96.44	18.90	19.59	25.5	16.12	130	875	0.124
97.94	20.00	20.42	26.0	16.65	174	916	0.096
97.14	38.40	39.53	26.0	32.24	222	964	0.145
97.44	62.50	64.14	26.0	52.31	267	1009	0.196
98.94	93.80	94.80	22.0	79.75	384	1125	0.208
96.94	110.30	113.70	26.0	92.73	533	1275	0.174
						Av.	0.157

The values of the ratio V/P are very erratic. If a graph be drawn from the values in columns five and six of Table XIII the points are scattered to such an extent that it is impossible to draw a representative line between them, hence the value for s_{25} cannot be determined.

The Relation of Supersaturation to Solubility

The graphs shown in the foregoing experiments show that *the supersaturation is approximately proportional to the pressure at which the saturation of the gas in the liquid took place.* Moreover, if the solubility of a given gas in a given liquid, as used in this investigation, be calculated for different pressures by means of Henry's law, and the solubility so obtained be plotted against the pressure, the resulting graph will be practically identical with the one obtained for the same gas and liquid in which the volume of gas shaken out at atmospheric pressure—the supersaturation—is plotted against the pressure at which saturation took place. In the case of carbon dioxide in water and alcohol this statement does not apply.

The rate of evolution of gases from supersaturated solutions is of considerable importance in connection with industrial and biological problems as has already been pointed out by Findlay and King.[1] This part of the problem will be further investigated.

Summary

1. An apparatus for saturating gases in water and various organic liquids at pressures ranging from one to five atmospheres is described.

This apparatus may also be used for determining the solubility of gases in liquids at different pressures.

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[1] Findlay and King: loc. cit.

2. Saturated solutions of the following liquids and gases have been prepared at pressures ranging from one to about five atmospheres:

Water, ethyl alcohol, acetone and carbon tetrachloride with oxygen.

Water, aniline, nitrobenzene, ethyl alcohol and benzene with nitrogen.

Water with air and hydrogen.

Water and ethyl alcohol with carbon dioxide.

After each liquid had been saturated with gas at the elevated pressure, the pressure above the liquid was reduced to that of the atmosphere and the supersaturated gas which remained in the liquid was shaken out and its volume determined.

The ratio of the volume so determined to the pressure at which saturation took place was found to be practically constant for any given gas and liquid. In the foregoing experiments, then, the supersaturation of the gas in the liquid is proportional to the pressure at which saturation took place.

3. The graph obtained by plotting the volumes of gas shaken out of a supersaturated solution against the pressures at which saturation took place, is nearly identical with the solubility-pressure graph obtained by Henry's law for the same gas and liquid. In other words, when these liquids are saturated at a high pressure and the pressure above the liquid is then reduced the *total amount* of gas corresponding to the difference in solubility between these two pressures remains in the supersaturated condition. Notable exceptions to this rule were found in the case of carbon dioxide in water and ethyl alcohol.

4. The rates with which the gases came out of the supersaturated solutions varied with the gas and liquid used. This will be the subject of further investigation.

Madison,
Wisconsin

STUDIES IN HETEROGENEOUS EQUILIBRIA. IV: THE SOLUBILITY OF STRONG ELECTROLYTES

BY J. A. V. BUTLER

Introduction

The solubilities of strong electrolytes in aqueous solutions have usually been discussed on the supposition that the solubility is determined by the equilibrium between solid salt and unionized molecules on the one hand and that between unionized molecules and their ions on the other. The law of solubility product in dilute solutions follows from the assumptions that the first of these equilibria is unaffected by the moderate addition of salts and that the second is governed by the law of mass action.[1] It is certain that the law of mass action does not apply to the ionization of strong electrolytes and in an exhaustive series of investigations by A. A. Noyes and his collaborators[2], it was shown that the second assumption is also incorrect and that both the solubility product and the concentration of unionized molecules, calculated on certain assumptions from the conductivity data, are far from constant. More recent investigations have been directed towards making appropriate modifications of the law of mass action, and to the thermodynamical device of determining the effective concentrations or activities which fit the thermodynamical equations.

At the same time it has become apparent from our knowledge of the polar structure of salt crystals that the solution of a salt is essentially an ionic process. In the solid salt, the molecule in the ordinary sense of the word does not exist. If the crystal is built up of ions acting as independent units in the lattice structure, there is no reason to suppose that the ions in the surface layer may not independently pass into solution and that ions from solution may not independently take their places in the crystal lattice.

It is the purpose of this paper to develop on kinetic grounds such a view of the independent solution of ions. On the basis of the statistical equations developed in the previous papers of this series[4] a general equation for the solubility of strong electrolytes is obtained, of which the law of solubility product is a special case. It is then shown that the relation between the heat of solution and the solubility product contained in this equation is confirmed by the available data.

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[1] Nernst: Z. physik. Chem. 4, 379 (1889); A. A. Noyes: Z. physik. Chem. 6, 243 (1890).

[2] A. A. Noyes, W. D. Harkins and others: J. Am. Chem. Soc. 33, (1911).

[3] See Lewis and Randall: "Thermodynamics" (1923); Brönsted: "Studies on Solubility" J. Am. Chem. Soc. 42, 671, 1448 (1920); 43, 2265 (1921); 44, 877, 938 (1922).

[4] Part I. Trans. Faraday Soc. 19 (1924). Parts II. and III. Discussion on "Electrode Reactions and Equilibria" held by Faraday Soc. Nov. (1923).

The Kinetics of the Solubility Process

It has long been known that salt crystals strongly adsorb a common ion from solution. While this has been appreciated analytically, the most convincing evidence has come from the study of the electric charges carried by colloidal particles of insoluble salts. Numerous examples of the stabilizing effect of a slight excess of a common ion on such suspensions are known[1]. In all such cases the sign of the surface charge is that of the common ion present in excess.

In a recent investigation Fajans and Frankenburger[2] have determined the amount of adsorption of silver ions by silver bromide crystals. They find that the number of silver ions adsorbed from a solution of silver nitrate of concentration 1.8×10^{-5} mols/litre in the presence of potassium nitrate is one for every four to ten bromide ions of the exposed surface of silver bromide. These authors recognized the intimate bearing of their results on the question of the solubility product and their remarks on this point may be quoted in full on account of their close connection with the more detailed treatment which follows.

"The crystal lattice of a salt adsorbs (in this case) one of the kinds of ions constituting it. The adsorption forces are here identical in nature with those holding the adsorbent together. The connection between such an alternate adsorption of both kinds of ions and the growth of a crystal from a supersaturated solution is easy to see.

"A very clear idea of the quantitative effect of an excess of one kind of ion on the solubility of a binary salt according to the law of mass action is thereby afforded. If we assume for simplicity a difficulty soluble salt, both of whose ions are equally strongly adsorbed on the same crystal lattice, i.e. in contact with the saturated solution containing both ions in equal concentration, there arises no potential difference between salt and solution. If we add now an excess of one of the ions, say the kation, the "adsorption equilibrium" of this ion on the anions of the lattice is disturbed, consequently it is deposited on the anions of the lattice covering them in part and giving the lattice a positive charge. The equilibrium with anions in solution is thereby also disturbed as can easily be seen from the facts that the anions of the lattice which are covered by positive ions are removed from kinetic contact with the solution and that the surface now carrying an excess positive charge exerts an increased attraction on the anions of the solution. Fresh anions must therefore be deposited on the crystal lattice from solution until a new state of equilibrium is set up with a smaller concentration of anions. This means that the solubility of the salt is lowered by an excess of kations. It is clear that a closer investigation of the whole adsorption isotherm for both ions must give a quantitative connection with the law of solubility product. Two points can already be seen. Firstly, since the adsorption of kations in the case considered is the greater,

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[1] Mukherjee: "The Physics and Chemistry of Colloids" General Report of a discussion by the Faraday Society and the Physical Society, 1920, 103 (1920).

[2] Z. physik. Chem. 105, 255, (1923).

the greater the excess added to the solution, so must the amount of anion precipitated increase likewise and the solubility decrease, corresponding entirely qualitatively with the law of mass action." Secondly, it is pointed out, it provides a connection between the law of solubility product and the Paneth adsorption rule.

We can accept this as a general picture of the process. But there is no reason for supposing that a crystal must adsorb both ions equally from its simple saturated solution. It may obviously happen that the tendency of one of the ions to go into solution may be greater than that of the other, owing either to a smaller attraction of the lattice or a greater attraction of the solvent for this ion. If, for example, the negative ion has the greater tendency to go into solution the surface will be left with an excess of positive ions and a potential difference will be set up whereby the solution negative ions is retarded and that of positive ions assisted. Eventually a state will be reached in which the ions are dissolved and deposited at equal rates.

The general case may be developed as follows:—

Confining ourselves to a binary electrolyte, let there be N ions of each kind per square centimetre of the crystal surface. When equilibrium is reached it may be supposed that the surface consists of an incomplete surface layer above a complete second layer of ions. Suppose that the incomplete surface layer consists of Nx positive ions and Ny negative ions. Each vacancy for a positive ion in the first layer discloses a negative ion underneath it and *vice versa.* Consequently the surface exposed to the solution is composed of N $(x+1-y)$ positive ions and N $(y+1-x)$ negative ions, giving it a net positive charge of $2N(x-y)$.

Let the potential difference corresponding to the work done against electric forces by a unit positive ion in reaching the surface from the interior of the solution be E. It is necessary to modify the solubility equations of Part I. in order to take account of the superposition of this electrical factor on the two solubility forces there considered for each of the ions.

The work done by a positive ion in reaching the "balance point" from the surface will now be $W_1-nE'F$, in reaching the same point from the interior of the solution $W_2+nE''F$, where W_1 and W_2 are the corresponding amounts of work done against the combined "solubility forces" and $E'+E''=E$.

The number of positive ions leaving the surface per square centimetre per second is therefore:

$$\theta_1=N\left\{1-(x-y)\right\} A'\sqrt{T}\,e^{-\frac{W_1-nE'F}{RT}} \qquad (1)$$

$$\text{where } A'=\nu\sqrt{R/W_1\pi}$$

Now a positive ion reaching the surface can only be fixed in quite definite positions, i.e. above uncovered negative ions. If we picture the surface as divided into positive and negative "squares" we see that on the supposition that a positive ion can only be held if it comes right within a negative square, the number of positive ions deposited per second is given by:

$$\Theta'_2 = N_s\left\{ 1-(x-y) \right\} A\sqrt{T}\, e^{-\frac{W_2+nE'F}{RT}} \qquad (2)$$

where N_s is the number of positive ions per cubic centimetre of the solution and $A=\sqrt{R/2\pi M}$.

If the localized attractive forces of the crystal lattice overlap the "squares" to some extent the number of ions condensed will be rather greater than Θ_2', say $\alpha\Theta_2'$. For equilibrium at the surface, we have then:

$$N\left\{ 1+(x-y) \right\} A'\sqrt{T}\, e^{-\frac{W_1-nE'F}{RT}}$$

$$=N_s\left\{1-(x-y)\right\}\alpha A\sqrt{T}\, e^{-\frac{W_2+nE'F}{RT}} \qquad (3)$$

That is:

$$N_s = N \left\{\frac{1+(x-y)}{1-(x-y)}\right\} \frac{A'}{\alpha A}\, e^{-\frac{W_2-W_1}{RT}+\frac{nEF}{RT}} \qquad (4)$$

For negative ions we obtain a similar expression:

$$N_s'=N \left\{\frac{1-(x-y)}{1+(x-y)}\right\}\frac{A_1'}{\alpha' A}\, e^{\frac{W_4-W_3}{RT}-\frac{nEF}{RT}} \qquad (5)$$

Multiplying (4) and (5),

$$N_sN^1_s = \frac{N^2A'A'_1}{A^2\alpha\alpha^1}\, e^{-\frac{W_2-W_1}{RT}+\frac{W_4-W_3}{RT}} \qquad (6)$$

Here $(W_2-W_1+W_4-W_3)$ is equal to the heat of solution of the salt U per gram molecule in saturated solution.

Introducing the molar concentrations of the ions

$$c= \frac{N_s}{N_0} \times 1000 \text{ and } c' = \frac{N_s'}{N_0} \times 1000, \text{ we obtain}$$

$$\ln(cc') \doteq \frac{U}{RT} + \frac{N^2A'A_1'10^6}{A^2\,\alpha\alpha^1\, N_0^2} \qquad (7)$$

We see that so long as the heat of solution is not affected by changes in the concentrations of salts in the solution and if α,α^1 remain constant, the product of the concentrations of the two ions in solution is constant. That is, under these conditions we have arrived at a kinetic deduction of the law of solubility product.

Evidence has already been presented in Part I. that the second term on the right of (7) leads to values which are at least of the right order of magnitude. We shall now consider the relation between the solubility product and the heat of solution U which is indicated by this equation.

The Dependence of the Solubility Product on the Heat of Solution

According to (7) the addition of any substance to the solution which affects the heat of solution, i.e. the attraction of the liquid for either of the ions will occasion a corresponding change in the solubility product.

Writing (7) in the form

$$\log_{10} P = \frac{U}{2.303\ RT} + K \qquad (8)$$

and assuming that K is independent of the temperature, for two temperatures T_1 and T_2 we obtain

$$\log_{10} \frac{P_1}{P_2} = \frac{U}{2.303\ R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{(1)} \qquad (9)$$

Consequently knowing the solubility product at two temperatures for a certain concentration of added substance we can calculate U, and proceed to test the validity of (8)[2]

It must be noted that such a relation has already been observed in one case for the effect of an electrolyte on the solubility of a non-electrolyte. McKeown[3] has shown from Thorne's data[4] that the solubilities of ether in sodium chloride solutions are related to the heats of solution by an equation analogous to (8), and suggested a statistical explanation couched in more general and vaguer terms than that of the author[5].

In attempting the verification of (8) for strong electrolytes with existing data two difficulties are met with.

In the first place there is the difficulty which has entered into all discussions of the solubility product, the uncertainty of the proper values of the ion concentrations. Following Brönsted[6] in the calculations given below, this difficulty has been avoided by the use of the total stoichiometrical concentrations of the ion species concerned, without any regard for the degree of dissociation. The "stoichiometrical solubility product" so obtained is of course not the same as that in which ion concentrations calculated according to any particular assumptions are used. A further discussion of this point is given after the calculations have been presented. Secondly, it is a matter for regret that practically all the accurate investigations on the solubility product particularly those in which parallel conductivity measurements were made, were carried out at one temperature only and therefore cannot be used for the purpose of testing this relation. Since a comparatively small error in solubility will give rise to a large error in the heat of solution, it is preferable to employ

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[1] This differs from the familiar isochore expression in that the Van't Hoff factor i must be introduced in the deduction of the latter. U is here the partial molar heat of solution.

[2] If the solvent does not contain a common ion $P = C^2$, and we shall use the simpler form

$$\log_{10} C. = \frac{U}{2 \times 2.303\ RT} + K'$$

[3] J. Am. Chem. Soc. 44, 1203 (1922).

[4] J. Chem. Soc. 99, 262 (1921).

[5] This paper did not come to the author's notice until recently and on that account was not referred to in the first paper of this series.

[6] J. Am. Chem. Soc. 42, 761 (1920).

measurements made under similar conditions and by the same workers at the two temperatures.

Few measurements have been found in the great mass of solubility data which are suitable for our purpose. Most of these have been calculated and the results are presented in Tables I to X.

In his extensive series of determinations of the solubilities of the complex ammines Brönsted has given the solubilities of four complex binary salts in water and in 0.2 M salt solutions[1] at 0° and 20°. These solubilities, together with the calculated heats of solution, and the values of K (equation 8) are tabulated in Tables I to IV. Table V gives the solubilities of β-"croceo" cobaltic nitrate in potassium formate solutions of different concentrations by the same author[2]. Table VI gives Brönsted's data for β-croceo nitrate in water and 0.1 N nitrate solutions[3].

The solubilities of salts in solutions containing various non-electrolytes and electrolytes have also been measured with some care at 0° and 25° by Armstrong and Eyre[4].

Some representative cases are given in Tables VII, VIII and IX. The solubilities are expressed by the authors as grams. salt per 1,000 grams water. The corresponding solubilities per 1,000 grams. solution were calculated and employed. The specific gravities of these solutions being unknown, it was not possible to give the true volume concentrations. If however, as may reasonably be supposed to be approximately the case, the ratio of the specific gravities of solutions of different compositions at the two temperatures is constant, the "U" obtained from the data will differ from the true value by a constant factor. Table X. gives the determinations of Touren[5] of the solubility of potassium chloride in potassium nitrate solutions of various strengths[6].

TABLE I

Xantho-cobaltic Tetrathio-cyanato-diammine Chromiate in Water and 0.2 M Salt Solutions

Solvent	Solubility $\times 10^6$		U	K′
	0°	20°		
H_2O	392	1284	−18900	4.18
$NaCHO_2$	629	1950	−18030	4.04
$KCHO_2$	667	2040	−17700	3.93
NaCl	680	2097	−17850	4.00
KCl	723	2193	−17430	3.86
$NaNO_3$	746	2228	−17330	3.83
KNO_3	790	2325	−17110	3.77

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[1] J. Am. Chem. Soc. 44, 886 (1922).

[2] J. Am. Chem. Soc. 43, 2276 (1921).

[3] Z. physik. Chem. 1922, 100, 139.

[4] Proc. Roy. Soc. 84A, 123 (1910).

[5] Compt. rend. 130, 909 (1900).

[6] The data of Armstrong and Eyre for this case appear to be somewhat irregular.

TABLE II

Xantho-cobaltic Tetranitro-diammine Cobaltiate in Water and 0.2 M Salt Solutions

Solvent	Solubility × 10^6		U	K′
	0°	20°		
H_2O	311	992	−18380	3.87
$NaCHO_2$	570	1692	−17230	3.68
$KCHO_2$	629	1824	−16860	3.57
NaCl	621	1823	−17060	3.64
KCl	682	1952	−16650	3.52

TABLE III

Chloropentammine Cobaltic Tetranitro-diammine Cobaltiate in Water and 0.2 M Salt Solutions

Solvent	Solubility × 10^6		U	K′
	0°	20°		
H_2O	173	637	−20640	4.53
$NaCHO_2$	325	1100	−19320	4.27
$KCHO_2$	363	1207	−19020	4.20
NaCl	353	1186	−19200	4.26
KCl	393	1291	−18850	4.16

TABLE IV

Chloropentammine Cobaltic Tetrathio-cyanato-diammine Chromiate in 0.2 M Salt Solutions

Solvent	Solubility × 10^6		U	K′
	0°	20°		
$NaCHO_2$	477	1516	−18550	7.45
$KCHO_2$	510	1592	−18020	7.24
NaCl	524	1627	−17950	7.21
KCl	548	1702	−17950	7.21

TABLE V

β-Dinitro-tetrammine Cobaltic Nitrate in Potassium Formate Solutions

Concentration of KOOCH	Solubility × 10^6		U	K′
	0°	20°		
0	494	1298	−15200	2.84
.05	575	1467	−14800	2.72
.1	621	1570	−14670	2.69
.2	693	1713	−14300	2.50

TABLE VI

β-Dinitro-tetrammine Cobaltic Nitrate in Water and Nitrate Solutions.*

	Solubility product × 10^6		U	K
	0°	20°		
H_2O	25.1	170.6	−15180	1.50
.1 KNO_3	44.3	262.4	−14100	1.31
.1 $NaNO_3$	44.1	249.8	−13740	1.22

*Brönsted (loc. cit.) gives the solubilities at a number of other temperatures between 0° and 20°. The mean values of U calculated for the temperature intervals 0−10.06, 10.06−20, 5.02−15.07, 0−20, are: H_2O, −15190; 0.1 KNO_3, −14090; 0.1 $NaNO_3$, −13840. It may be noted that in his discussion on the effect of temperature on solubility etc. Brönsted assumes that the heat of solution in water is the same as in 0.1 nitrate solutions. He gives in support a calorimetric determination of the heat of solution in water, giving the value −14150 cals. which differs appreciably from the solubility values.

TABLE VII

Potassium Chloride in Methyl Alcohol Solutions

Alcohol Mols/1000 gms	Solubility. Gms/1000 gms. solution		U	K′
	0°	25°		
0	221.0	267.0	−2440	3.32
.25	217.3	264.2	−2514	3.35
.50	213.8	260.0	−2523	3.34
1.00	206.0	252.6	−2627	3.37
3.00	178.4	228.3	−3170	3.52

TABLE VIII

Potassium Chloride in Propyl Alcohol Solutions

Alcohol Mols/1000 gms	Solubility. Gms/1000 gms. solution 0°	25°	U	K′
0	221.0	267.4	−2454	3.33
.25	212.7	259.3	−2560	3.35
.50	205.0	252.3	−2680	3.39
1.00	189.7	238.2	−2940	3.46

TABLE IX

Potassium Chloride in Hydrochloric acid Solutions

HCl Mols/1000 gms.	0°		25°		U	K
	KCl Mols/1000 gms.soltn.	P	KCl Mols/1000 gms soltn.	P		
0	2.962	8.775	3.545	12.56	−2315	1.87
.25	2.807	8.581	3.391	12.35	−2344	1.88
.5	2.643	8.305	3.239	12.11	−2430	1.89
1.0	2.296	7.570	2.929	11.51	−2700	1.94

TABLE X

Potassium Chloride in Potassium Nitrate Solutions

KNO_3 Mols/litre	14.5°		25.2°*		U	K
	KCl Mols/Litre	P	KCl Mols/Litre	P		
0.0	3.865	14.94		17.48	−3128	3.07
.204	3.810	15.29		17.69	−2813	2.95
.318	3.782	15.51		17.86	−2244	2.90
.615	3.710	16.05		18.35	−2131	2.83
.910	3.629	16.47		19.00	−2265	2.94
1.220	3.582	17.20		19.51	−2000	2.78

*By interpolation.

It will be seen that Tables I to V deal with the effect on the solubility of additions of electrolytes not containing a common ion, Tables VII and VIII with additions of non-electrolytes and Tables VI, IX and X with additions of electrolytes with a common ion. Further the salts concerned include extremely complex binary ammines of comparatively low solubility and the fairly soluble simple salt KCl.

In all cases the effect of the addition of other substances to the solution, with or without a common ion, on the solubility product is uniformly parallel with the effect on the heat of solution. A few irregularities may be observed, but these may be ascribed to errors in the solubility data. The quantity K is not quite constant and its uniform change with the heat of solution indicates a real change. It must be remembered that this quantity besides including the indeterminate factors α,α' contains the terms A,A′ which depend on W_1 and W_3, unknown parts of the total heat of solution.

It was pointed out earlier that the solutions and solubility products given are stoichiometrical quantities, no attempt being made to introduce the degree of dissociation. The uniformity with which the introduction of these quantities in the equation represents the effect on the solubility of additions of such different kinds makes it possible to suggest tentatively that it is the "total ion concentration" which functions in the solubility process of strong electrolytes. A thorough investigation of a particular case is necessary before pronouncing definitely. In view of the important bearing of this point on the theory of complete dissociation, it is intended to undertake such an investigation.

With regard to the connection between the heat of solution and the composition of the solution, it may be observed that Brönsted has referred many of his measurements to the equation $\ln(c_1c_2) = 2\alpha\sqrt[3]{C_t} + \text{const.}$, where C_t is the total ion concentration.

If our relation (8) is correct this implies that $U \propto \sqrt[3]{C_t}$. On the other hand Rothmund's equation $1/c \log\frac{n_1}{n_2} = \beta$ indicates that the change in the heat of solution is approximately proportional to the concentration of added substance. Some preliminary calculations on the scanty data available indicate that neither of these relations represents the effect very well and the matter may be left for further study.

The relation of our equations and the conception of activities may also be briefly indicated. Let activity co-efficients f_1f_2 be introduced so that $C_1C_2f_1f_2 = k$ in any solution.

$$\text{If } (C_1C_2) = \frac{U}{RT} + K \text{ we see that}$$

$$(f_1f_2) = \frac{U_0}{RT} - U + K_0 - K$$

where U_0 and K_0 refer to the standard state, and we may write for each ion

$$f = \frac{U'_0 - U'}{RT} + K'_0 - K'.$$

Summary

1. The kinetics of the solubility of strong electrolytes is developed and a general equation for the solubility of a binary salt is obtained which includes the law of solubility product as a special case.

2. It is shown that the relation between the solubility product and the heat of solution included in this equation is amply confirmed by the available data.

3. The connection between this treatment and (1) the theory of complete dissociation of strong electrolytes in solution, and (2) the conception of activities is discussed.

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DISPERSITY OF SILVER HALIDES IN RELATION TO THEIR PHOTOGRAPHIC BEHAVIOR[1]

BY FRANK E. E. GERMANN AND MALCOLM C. HYLAN

Introduction

There has been of late considerable discussion among photographic chemists over the relation between size of the silver halide grain and the speed of the photographic plate. Wightman, Trivelli and Sheppard[2] seem to find that the relative speed of emulsions increases rapidly with the average size and range of size of the particles contained therein. That this is not always true is shown by the following[3]: "An experimental emulsion was prepared, the grains of which measured up to 8μ in diameter and which had an H and D speed of only 38. In comparison with this emulsion a Royal Standard Lightning Plate from Kodak Ltd. was tested, the grains of which averaged up to 2.8μ in diameter and of which the H and D speed was 728. Thus it appears that emulsions containing grains of approximately 1/3 the linear dimension are more than 19 times as sensitive. This is also true of individual grains in the same emulsion".

Koch and du Prel[4] have concluded that it is not possible, with the information at present available, to formulate a definite relation between grain-size and sensitivity, but that it is certain that the largest grains in an emulsion are by no means the most sensitive.

Before going on to a further discussion of the experimental results obtained by various authors it will be well to consider, from a purely theoretical standpoint, what should be expected.

If we accept the sub-halide theory of the photochemical action of light on the silver halide, the *amount of halide* affected in unit time becomes the determining factor in the speed of the plate. If we accept the nuclear theory it is the *number of grains* affected which determines the number of nuclei formed and therefore the speed of the plate. Supposing light to have a continuous wave-front, that is, *not* a quantum-like or discrete structure of radiation, then the *amount of halide* affected would depend upon the "effective area" of the particles, and the *number of particles* affected would depend upon their "relative number". By "effective area" is meant the sum of the projectional areas of the particles. By "relative number" of particles is meant the number of particles present per unit weight of silver halide. Now both "effective area" and "relative number" are proportional to the dispersity. This will be readily seen from the following illustration. We may consider the grains to approxi-

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[1] Extract from a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] J. Phys. Chem. 27, 1-51 (1923).

[3] Eastman Kodak Co. Monographs on the Theory of Photography No. 1, p. 104.

[4] Physik. Z. 17, 536 (1916).

mate spheres. Suppose, then, we have a sphere of radius R. Its mass will be $4/3\pi R^3\rho$, where ρ is the density. Its projectional area will be πR^2. Let us, then, take an equal mass of spheres of radius $r = R/2$. Then the mass of each sphere will be $4/3\pi r^3\rho$ or $1/8$ of the larger sphere. We will then have 8 small spheres. The projectional area of each will be πr^2, and their total projectional areas will be $8\pi r^2$ or twice the projectional area of the large sphere. It is evident, then, that by halving the linear dimensions we double the "effective area" and mutiply the number of particles by 8, or to be more general, the "effective area" is inversely proportional to the linear dimensions of the particles, and the number of particles, or "relative number", is inversely proportional to the cube of the linear dimensions.

Suppose, now, we consider light to consist of quanta, or discrete particles of radiation. Then the probability of each quantum coming in contact with silver halide will be proportional to the "effective area", and while greater dispersity will reduce the probability of any single particle being hit, it will increase the probability of the quantum hitting some silver halide. Thus the *amount of halide* affected is again proportional to the dispersity. And, finally, the number of particles hit will also be greater the greater the dispersity.

Let us suppose that instead of the number of particles affected it is the number of molecules affected which is the determining factor. Owing to photochemical extinction, the amount of light reaching any molecule will depend upon its distance from the surface of the particle. Here again the greater the dispersity the more molecules are at or near the surface. For example take the spheres used as an illustration above. Light of sufficient intensity to just penetrate to the center of the small spheres would penetrate but half way to the center of the larger one.

Thus, viewed from a number of different angles, theoretically it would seem that the smaller-grained emulsions should be the faster. The apparent usual greater speed of coarse-grained emulsions must be due to factors other than purely dimensional ones.

The work of the authors on the speed of silver iodide emulsions[1], in which they found the apparent great difference between the speed of iodide and bromide to be due principally to the adsorption of potassium iodide by the former, led them to wonder if the apparent greater speed of coarse-grained emulsions, in direct opposition to the theoretically expected result, might not be due to a similar phenomenon. Assumption of such a cause for the discrepancy between theory and practice perfectly explains the experimental results obtained by many investigators. We will take up some of these in detail.

We should expect, since in gelatin emulsions the silver halide is formed in the presence of excess soluble halide[2], that the finer grained emulsions would contain much more adsorbed halide, the effect of which might neutralize, or

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[1] Germann and Hylan: J. Am. Chem. Soc., 45, 2486 (1923).

[2] Eastman Monograph, No. 1, p. 27.

even reverse, the purely dimensional effect of the grains. To quote Trivelli and Sheppard[1], "The smaller the crystal, the larger its relative surface, and the more it is liable to contamination with dissolved and adsorbed foreign molecules." In an emulsion, then, containing considerable excess of soluble halide we should expect the speed to be inversely as the adsorbed halide, or, in other words, directly proportional to the grain size. Probably the difference Wightman, Trivelli and Sheppard[2] found between their own experimentally prepared emulsions and the Royal Standard Lightning Plate from Kodak Ltd. lies here, in the difference in excess of soluble halide.

The effect of variation of size can also be explained by adsorption. Adsorption, in general, is proportional to the "specific surface" of the adsorbent. "Specific surface", which may be defined as the surface per unit mass of material, is proportional to the dispersity. Again taking spheres as examples, a sphere of radius R would have a surface of $4\pi R^2$. As we have shown above, if we take an equal mass of spheres of radius $r = R/2$ we would have 8 small spheres. The surface of each would be $4\pi r^2$, and the total surface of the 8 would be twice that of the single large sphere. Thus the specific surface is inversely proportional to the linear dimensions of the particles. We have taken spheres as examples because they have less surface per given mass than any other solid figure, and hence the ratios we have developed for them are a minimum. If the crystals were very irregular in shape the increase of surface per decrease of linear dimensions might be considerably greater. In emulsions, then, having considerable range in the size of the particles, the smaller grains, present together with the larger ones, adsorb relatively more halide and leave the larger ones relatively purer than if there were only large ones present.

The "ripening" effect of allowing emulsions to stand at room temperature or higher for some time before use has been thought by some to be due to increase in size of grain, similar to "digesting" a barium sulfate precipitate before filtering. But to again quote Trivelli and Sheppard[3], "modern high-speed emulsions, relatively coarse grained, are not produced by the ripening of emulsions which would otherwise be slow and fine grained. The two types are produced under relatively different initial conditions, and, as pointed out by Lüppo-Cramer and Mees, are practically discontinuous." And again, "ripening by way of recrystallization depends mainly on the elimination of adsorbed impurities."

As adsorption phenomena are more accentuated in silver iodide than in other silver halides, a study of the relations between size of grain and sensitiveness in plates of this material seemed worth while.

Experimental

Various methods were attempted for preparing simultaneously two emulsions, of which one would contain relatively small, and the other relatively

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[1] Eastman Monograph, No. 1, p. 29.

[2] J. Phys. Chem. 27, 1-51 (1923).

[3] Eastman Monograph, No. 1, p. 27.

large particles of silver halide. The method finally found to be most successful for obtaining fine-grained emulsions consists, in general, of mixing concentrated solutions of silver nitrate and potassium halide. The most successful method for preparing coarse-grained emulsions consists of adding the required amount of crystalline silver nitrate to a dilute solution of potassium halide, and stirring the mixture only after the nitrate and halide have had time to react.

In order to get a fair comparison of the effect of size of halide grain on the speed of the emulsion, the emulsions compared must contain equal weights of silver halide. The maximum amount of silver which could be deposited from each would be the same. The excess of potassium halide in the two emulsions must also be equal in order to give equal Mass Action effects. Taking these facts into consideration, emulsions were prepared as described below.

For the fine-grain emulsion 5gm of silver nitrate and 5gm of potassium iodide were accurately weighed on the balance. The potassium iodide was dissolved in 5cc of distilled water, together with something less than a gram of gelatin. The silver nitrate was dissolved in 3cc of distilled water and quickly added to the gelatin-potassium iodide solution. The resulting silver iodide emulsion was then added to 240cc of distilled water in which 20gm of gelatin had previously been dissolved, and the whole stirred vigorously to insure thorough mixing.

For the coarse-grain emulsion 0.5gm of silver nitrate and 0.5gm of potassium iodide were accurately weighed. The potassium iodide was dissolved in 25cc of distilled water, together with 2gm of gelatin. When solution was complete the crystalline silver nitrate was added, and, after allowing time for the reaction of the iodide and the nitrate, the emulsion was thoroughly stirred.

A slide for microscopic examination was prepared from each emulsion by pouring some of the warm fluid emulsion over the slide, rotating it to get it to spread evenly over the surface, and pouring off the excess. The emulsions were then painted on cards and set away to dry.

When dry, a card from each was exposed for one minute and developed for five minutes in alkaline metol solution. In each case, the card having the large grains gave a fair picture, while the card having the small grains gave a faint picture or no picture at all.

A card from each emulsion was bathed for five minutes in metol sulfite sensitiser, dried, exposed for one second, and developed in alkaline sulfite solution for 30 seconds. In each case the card having the smaller grains gave much the better picture. For details as to the metol sulfite sensitiser, the alkaline sulfite developer, and the alkaline metol developer the reader is referred to a previous article by the authors[1] on "The Photographic Sensitiveness of Silver Iodide".

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[1] Germann and Hylan: J. Am. Chem. Soc. *l. c.*

Photomicrographs of several of the experimental emulsions were also taken to serve as a record. The equipment used consisted of a Bausch and Lomb photomicrographic bench, mounted on a concrete pier to reduce vibrations to a minimum. The illumination was furnished by a 5 ampere hand-feed arc light, fitted with a Bausch and Lomb aspheric condensor, and a Wratten filter. The microscope was a Spencer, fitted with a 4mm oil-immersion 1.25NA objective, a 10X Huygens occular, and a Spencer 1.3NA substage condensor. The pictures were taken on Wratten M plates.

Discussion

It is to be noted that in every case where a distinct difference in the average grain size was observed, the emulsion having the coarser grains was the faster if not sensitised, but that the finer grained emulsion was the faster after sensitisation. This is in perfect harmony with the theoretically expected results as discussed in the introduction.

The authors[1] in their article on "The Photographic Sensitiveness of Silver Iodide" have shown that the principal effect of sensitising these emulsions is the removal of adsorbed potassium iodide. In the unsensitised emulsion, then, the excess of potassium iodide is adsorbed on the silver halide grains, and the smaller grains adsorbing relatively more than the larger ones are retarded much more, so that, naturally more sensitive, they are actually rendered less sensitive than the larger grains. In the case of the sensitised emulsions the adsorbed potassium iodide has been removed and the relative sensitiveness of the large and small grains appears in its true light. As should be expected, the smaller-grained emulsions show the greater speed.

Svedberg[2] has found that the percentage number of grains made developable after a certain exposure increases approximately exponentially as the cross section of the grains increases. He claims, however, that this rule holds only for grains formed under very nearly the same conditions, such as the grains within one and the same emulsion. He assumes that the product of the light action in the halide grain consists of small centers distributed thru the grain, or thru the light-affected part of the grain, according to the laws of chance, and explains his experimental results in the following manner.

"A certain grain will become developed if it contains one or more developable centers. Now according to the laws of chance the percentage probability for the occurrence of *n* centers in a grain is

$$P_n = 100 \frac{e^{-v} v^n}{n\,!} \qquad (1)$$

where *v* is the average number of centers per grain. Thus the percentage probability that the grain will contain at least one center is

$$P = 100\ (1 - e^{-v}) \qquad (2)$$

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[1] Germann and Hylan: J. Am. Chem. Soc. *l.c.*

[2] Phot. Jour. 62, 186 (1922).

"The haphazard distribution of the centers thus explains the fact that not all of the grains of a certain size are made developable by a certain exposure, or in other words, it accounts for the fact that the characteristic curve for a certain class of equally sized grains is not merely a vertical line.

"If all the grains of an emulsion are built up of the same kind of light-sensitive silver bromide material, *v* in formula (2) will increase with the size of the grains and therefore also the percentage of developable grains, just as is found experimentally. The rapidity of the increase of *v* with size of grain would depend upon two factors: the ability of the developer to penetrate into the grain, and the homogeneity of the field of light in the grain. If the developer is not able to get into the interior of the grain, but only attacks the surface layer, then *v* would mean the number of centers in that surface layer and therefore *v* would increase in approximate proportion to the grain surface even in cases where the field of light in the grain was not homogeneous (because of strong light absorption). On the other hand, if the developer is to penetrate the grain, *v* would depend upon the field of light in the grain. If the absorption of light were feeble, *v* would increase in proportion to the volume of the grain; if the absorption were very strong *v* would increase approximately proportionally to the cross-section of the grain. The percentage of developable grains would in these various cases increase exponentially as a function of either surface, volume, or cross-section of the grains."

We shall now explain Svedberg's results on the basis of adsorption, and point out some faults in his theory. He states that in the higher sized classes of grains the shapes were thin discs whose volumes were approximately proportional to the cross-section. Now specific surface is proportional to the ratio of surface to volume, or expressed mathematically,

$$\text{Specific surface} = k\frac{s}{v}$$

where k is the reciprocal of density. This may be written

$$\text{Specific surface} = k \cdot s \cdot \frac{1}{v}$$

from which we may state that specific surface is inversely proportional to volume. Now adsorption is proportional to specific surface, and as developability is an inverse function of the amount of adsorbed retarder, we may say that developability is an inverse function of specific surface, or a direct function of volume. Hence we arrive at the same result as Svedberg, but from entirely different premises. The fault of Svedberg's theory is that while the probability of any single grain being affected by light increases with the size of that grain, if we take equal weights of silver halide, which is essential in getting a fair comparison of the speeds of two emulsions, the probability of *some* halide being affected is increased with the dispersity, as we have already shown. To prove his theory he submits photomicrographs of silver halide grains before exposure, and of the nuclei formed from them by partial development. It is to be noted, however, that these particles show no definite relation between the size of the original grain and the size or number of nuclei formed therefrom, as some of the smaller grains show nuclei while some of the larger ones show none, and some of the small grains show large nuclei while some of the large grains show but small ones.

Furthermore, since, as we have shown, the specific surface decreases in proportion as the diameter of the grains increases, or as the square root of the cross-section, assuming the grains to be spherical, it is quite likely that with increasing irregularity in the shape of the grains a condition is approached where the specific surface would vary inversely as the cross section of the grains. Now developability is inversely proportional to adsorbed retarder, adsorbed retarder is proportional to specific surface, and the concentration function is a generalized parabola. Hence we might expect that under the conditions assumed above developability might be a function of cross-section, as Svedberg's experiments seem to indicate, especially as he claims that this holds true only "for grains formed under very nearly the same conditions, such as the grains in one and the same emulsion," where adsorption conditions would be identical.

A further confirmation of our views is furnished by a method used in sensitising autochrome plates[1]. It has been found that a very small quantity of silver chloride in dilute ammonium hydroxide added to the orthochromatising bath increased by thirty times the sensitiveness of the autochrome plates of 1912. The cause is clear. The silver chloride reacted with the potassium bromide or potassium iodide adsorbed on the silver halide grains, leaving them free.

On the basis of adsorption we can explain, too, the great increase of speed in a bromide plate partially converted into iodide. Renwick[1] says of this, "When the silver bromide of a dry plate is converted to iodide the clear sharp-edged crystals. . . apparently become a more or less confused aggregate of either amorphous or micro-crystalline silver iodide." Clearly the dispersity is greatly increased, and there being an excess of silver bromide over the soluble iodide the latter is practically entirely used up, resulting in a crystal surface on the silver iodide practically free from adsorbed retarder.

We conclude, then, that, intrinsically, small-grained emulsions are faster than large-grained emulsions; that variations from this rule are due to adsorbed impurities, principally soluble halide; that sufficient adsorbed halide may neutralise or completely reverse the purely dimensional effect of the grains; and finally, that unless one knows not only the relative grain size but also the relative amounts of adsorbed halide in the two emulsions it is impossible to predict which will be the faster.

For his kind assistance in the preparation of the photomicrographs we wish to express our appreciation to Prof. Robert Canfield, of the Department of Civil Engineering.

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[1] Bull. Soc. franç. Phot.[3] 9, 90-92 (1922).

[1] J. Soc. Chem. Ind. 39, 156T, (1922).

Summary

1. It is shown that from purely theoretical considerations small-grained photographic emulsions should be faster than large-grained emulsions.

2. The apparent variations from this rule are explained on the basis of adsorption of soluble halide.

3. Adsorption phenomena being more accentuated in silver iodide than in other silver halides, a study of emulsions of this material is undertaken.

4. Methods are described for preparing large-grained and small-grained emulsions.

5. Among unsensitised emulsions the ones containing the larger grains are found to be the faster.

6. Among sensitised emulsions the ones containing the smaller grains are found to be the faster

7. It is concluded that, in ordinary photographic emulsions, owing to adsorbed impurities, it is impossible to formulate any relationship between grain-size and sensitiveness, but that among emulsions free from adsorbed retarders the ones containing the smaller grains are the faster.

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STUDIES IN ADSORPTION, PART VI

A New Interpretation of the Schulze-Hardy Law and the Importance of Adsorption in the Charge Reversal of Colloids.

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Adsorption and Schulze-Hardy Law

In some recent papers we had occasion to study the coagulating power of different electrolytes on manganese dioxide sol and also the adsorption of electrolytes by hydrated manganese dioxide both in course of precipitation and as well as by freshly precipitated and air dried solid free from all impurities.[1] It has been shown in these communications that in the coagulation of manganese dioxide sol, the Schulze-Hardy Law which establishes a relation between the coagulating power and the valency of the coagulating ion is but partially followed. It has also been definitely proved experimentally that in the adsorption of various electrolytes by precipitated manganese dioxide the ions most effective in coagulation are least adsorbed. Thus the coagulating power of silver ion is about 1/5 of that of mercuric ion, whereas its adsorption by precipitated manganese dioxide is about six times that of mercuric ion. Similar results have also been found with the air dried sample.

From a survey of the literature on the subject we find that up till now the Schulze-Hardy Law has not been rightly interpreted in explaining the experimental results on coagulation and adsorption. In this paper we have given a new interpretation of the above Law and we are of opinion that our interpretation can consistently explain the experimental results on coagulation and adsorption. In this connection we have also discussed the question of charge reversal from general principles based on experiments on adsorption.

The relation between the valency of ions and their coagulating powers have formed the subject of a large number of investigations. Experiments on these lines led to the generalisation known as Schulze-Hardy Law namely the higher the valency of an ion the greater is its precipitating action. The researches of Linder and Picton[2] on colloidal arsenious sulphide lent powerful corroboration to this Law.

The actual nature of coagulation of a sol by electrolytes is still obscure. Many workers in this field have sought to explain the mechanism of the coagulation process on the assumption that the addition of electrolytes destroys the potential of the Helmholtz double layer, which exists between the suspended particles and the medium. The theory which is now generally

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[1] Compare Ganguly and Dhar: J. Phys. Chem. 26, 701, 836 (1922): Chatterji and Dhar: Kolloid-Z. 33, 18 (1923.)

[2] J. Chem. Soc. 67, 63 (1895).

accepted is that of Freundlich[1] who assumes that preferential adsorption of one ion of the electrolyte by the colloid particles neutralises the charge carried by them and thus destroys wholly or partially the electrical double layer. These neutral particles come in contact with each other due to surface forces and, since the surface energy of a system always tends to diminish, they form bigger particles and are thus coagulated. Experimental support to this theory was obtained from Linder and Picton's work on arsenious sulphide sol, who observed that when colloidal As_2S_3 is coagulated with a solution of barium chloride, the filtrate becomes acidic and an appreciable amount of barium is carried down by the coagulated mass. This selective adsorption of ions from an added electrolyte by sols has been observed by many workers. Whitney and Ober[2] carried out some quantitative determinations of the amounts of certain ions adsorbed by colloidal As_2S_3 in course of precipitation and concluded that the amount of an ion carried down by a colloid is independent both of the concentration of the colloid and electrolyte; and that equivalent amounts of different ions are carried down by the same weight of the precipitate. This simple relation was very suggestive and on the basis of these experiments by Whitney and Ober and on his own work on the adsorption of several organic ions, Freundlich[3] assumes that, in the coagulation of a colloid, equivalent amounts of precipitating ions are carried down by the same weight of colloid. From this assumption he deduced that the most readily adsorbed ion precipitates in the lowest concentration and *vice-versa*. In order to test his views Freundlich made some experiments on the coagulative power of several electrolytes on colloidal arsenious sulphide and their adsorption by the colloid in the course of its precipitation.

He used the following electrolytes:—

Aniline hydrochloride, morphine hydrochloride, para-chlor aniline hydrochloride, strychnine nitrate, new magenta, uranyl nitrate, ceric nitrate, etc. In all cases the adsorption was comparatively small and by comparing the adsorption isotherms for different salts with the coagulating powers of the same salts, considerable variation was observed. Thus the coagulating power of strychnine nitrate was far less than that of aniline hydrochloride, parachlor aniline hydrochloride and morphine hydrochloride; but the adsorption of strychnine nitrate by the same amount of coagulated As_2S_3 was considerably greater than that of any of them. Again the coagulating power of parachloraniline hydrochloride was 2.5 times greater than that of aniline hydrochloride; but the adsorption isotherms practically coincided throughout, showing that aniline hydrochloride which had a less coagulating power was also equally adsorbed. Further in the case of uranyl and cerium ions he found that the amount adsorbed in milli-equivalents was about thirty percent more for uranyl ion than for ceric ion, though the coagulating power of ceric ion was

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[1] Kolloid-Z. 1, 321 (1907).

[2] J. Am. Chem. Soc. 23, 842 (1901).

[3] Kolloid-Z. 1, 321 (1907).

about nine times greater than that of uranyl ion. Freundlich's further experimental work on the adsorption and coagulating power of an ion on a sol shows greater divergence between these two factors.

Freundlich and Schucht[1] determined the precipitation value for colloidal mercuric sulphide and the amount of adsorption in the region of precipitating concentration. The adsorption was determined for metallic cations NH_4, Ag, Ba, Cu and Ce, and for dye cations New Magenta, Brilliant Green, Auramine and Methylene Blue. The results are given in the following table:—

Cations.	Precipitation value.	Adsorption at precipitation value. Milli-equivalents.
NH_4	10.2	.05)
Ba	.51	.044
Cu ($Cu(NO_3)_2$)	.15	.03
Cu ($Cu SO_4$)	.26	.22
Ag.	.28	.02
Ce	.082	.012
Auramine	.094	.011
New Magenta	.097	.008
Methylene Blue	.097	.007
Brilliant Green	.048	.004

A perusal of the table shows that the results disprove the assumption that equivalent amounts of ions are adsorbed at the precipitating concentration. Freundlich recognised this fact but he attributed the variation to the difficulties and errors of experiments. It should at once be pointed out that assuming the correctness of the results obtained, the data show a remarkable fact that the ion having the greatest precipitation value is also adsorbed most and *vice-versa*. This conclusion is exactly the opposite of that of Freundlich.

In order to further study the relationship between the coagulating power of ions and their adsorbability by a sol, Ishizaka in Freundlich's laboratory[2] made some experiments on the adsorption and coagulation of colloidal aluminium hydroxide. By examining the isotherms in which the adsorption values are expressed in moles the order of adsorption of anions appears to be salicylate > ferrocyanide > oxalate > chromate > tartrate > sulphate > chloride > nitrate > thiocyanate > sulphanilate, while the coagulating powers are in the order of ferrocyanide > sulphate > oxalate > tartrate > chromate > salicylate > chloride > nitrate > thiocyanate > sulphanilate. These results indicate that ions of greater valency have high coagulating value and at the same time they are highly adsorbed. Recent experiments, however, of Weiser and Middleton[3] on the adsorption of ions by aluminium hydroxide sol are not in agreement with the above. These results will be discussed later on.

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[1] Z. physik. Chem. 85, 641 (1913).

[2] Z. physik. Chem. 83, 97 (1913).

[3] J. Phys. Chem. 24, 630 (1920).

In a recent paper Gann[1] determined a few adsorption values for the precipitation of aluminium hydroxide sol. Only five ions were examined and the object of the experiment was to test Freundlich's theory that equivalent amounts of ions are adsorbed at precipitating concentration. The following table gives the results:—

Ion.	Precipitation value Millimole per litre.	Adsorption value at precipitation concentration.	
		In Millimoles.	In Milli-equivalent
Salicylate.	8	.30	.30
Picrate.	4	.18	.18
Oxalate.,	.36	.18	.36
Ferricyanide.	.10	.09	.27
Ferrocyanide.	.08	.073	.29

If we consider the results given in column 3, viz., amount of adsorption expressed in millimoles we immediately find that the greater is the precipitation value of an ion the greater is the absolute amount of adsorption. Moreover, another interesting fact is also observed that the greater is the valency of an ion the less the absolute amount of adsorption. Thus in this case the valencies of the ions varying from four to one show a variation in the absolute amount of adsorption from .073 to .30 millimole.

In recent years Weiser[2] and his collaborators have studied the adsorption of various ions by precipitating barium sulphate, aluminium hydroxide, and ferric hydroxide in presence of excess of several salts. From the results of their investigations the order of adsorption of ions by precipitating $BaSO_4$ is ferrocyanide > nitrate > nitrite > chlorate > permanganate > ferricyanide > chloride > bromide > cyanide > sulphocyanate > iodide, the ferrocyanide ion being adsorbed the most and the iodide the least. If the adsorption values given above are expressed in gram anions instead of gram equivalent anions the order becomes nitrate > nitrite > chlorate > ferrocyanide > permanganate > chloride ferricyanide > bromide > cyanide > sulphocyanide > iodide, the nitrate ion being adsorbed most iodide the least. Weiser and Sherrick (*loc. cit.*) remark that there is nothing even to suggest the Schulze-Hardy Law in the case of barium sulphate as an absorbent. It will, however, be observed here that in the latter method of tabulation both the ferrocyanide and ferricyanide ions are considerably less adsorbed than many of the monovalent ions though their valencies are higher.

In the second of the series of papers Weiser and Middleton (*loc. cit.*) determined the adsorption of several anions by precipitating a ferric hydroxide sol. This work is interesting from another point of view. The adsorption values have been determined at the precipitating concentrations of electrolytes and

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[1] Kolloid-Chem. Beihefte. 8, 63 (1916).

[2] J. Phys. Chem. 23, 205 (1919); 24, 30, 630 (1920); 25, 399 (1921).

as such a comparison can be made between the coagulating power of the electrolyte and the amount actually adsorbed by the coagulating mass. Their results are given in the following table:—

Anion.	Adsorption value		Precipitation Value
	Milligram anions.	Milliequivalent anions.	
Phosphate.	.5721	1.7165	.875
Citrate.	.5018	1.5046	.500
Tartrate.	.6232	1.2464	.475
Oxalate.	.4364	.9128	.525
Sulphate.	.3804	.7609	.485
Iodate.	.7512	.7512	.600
Dichromate.	.1559	.3119	.200

In the discussion of their results the above authors remark: "From the table it will be seen that all the ions are strongly adsorbed by hydrous ferric hydroxide; the amounts varying in milliequivalents per gram from approximately .3 in the case of dichromate to 1.7 in the case of phosphate ion. The average adsorption value in milliequivalents per gram of arsenic trisulphide was found by Whitney and Ober and by Freundlich to be approximately .08; and the average value per gram of mercuric sulphide was but .02. The values for hydrous ferric oxide show clearly that the amounts of ions carried down by a precipitated colloid are not equivalent. As a matter of fact the actual variation in the values is less than that noted by Freundlich with mercuric sulphide; but he attributed the variation from equivalents to the analytical difficulties connected with the determination of very small adsorption values. The relatively large adsorption values in the case of hydrous ferric hydroxide and the accuracy with which they may be determined indicate conclusively that the values are not even approximately the same. As before explained other conditions remaining the same equivalent amounts must be adsorbed to neutralise the charge on the colloidal particles; but the adsorption does not stop with the neutralisation of the charge and the amounts actually carried down by the precipitate will vary with the adsorbability of the ions.

"If the ions are arranged in the order of their adsorption values expressed in milliequivalent anions per gram of adsorbent the following series is obtained:

"Phosphate > citrate > tartrate > oxalate > sulphate > iodate > dichromate, the phosphate being adsorbed the most and the dichromate the least. The precipitation values expressed in milliequivalent per litre would indicate the order of adsorption to be:

"Dichromate > tartrate > sulphate > oxalate > citrate > iodate > phosphate. It is evident that there is a tendency for ions with the lowest precipitating values to be adsorbed the least and *vice-versa*, which is diametrically opposed to what one should expect. Since the ionisation constant for the third step in the ionisation of both citric and phosphoric acids is very small it might seem preferable to consider them as dibasic acids rather than tribasic.

The only change that this would make in the series of adsorption values would be to put tartrate ion ahead of citrate and phosphate ions, the series becoming:

Tartrate > phosphate > citrate > oxalate > sulphate > iodate > dichromate.

Under these conditions the precipitation values would indicate the order to be—

Dichromate > citrate > tartrate > sulphate > oxalate > phosphate > iodate.”

In the third paper Weiser and Middleton (*loc. cit.*) have made a quantitative determination of the coagulating power as well as the adsorption of several ions at the precipitating concentration by colloidal aluminium hydroxide. A few of the results are given below:—

Anion.	Precipitation value Millimoles per litre	Adsorption per gram Al_2O_3 Milligram anion.
Ferrocyanide.	.094	.3202
Ferricyanide.	.133	.4046
Sulphate.	.269	.4984
Oxalate.	.350	.5710
Phosphate.	.346	.8088

It will be seen from this table that the order of adsorption is phosphate > oxalate > sulphate > ferricyanide > ferrocyanide the phosphate ion being adsorbed the most and the ferrocyanide the least. Arranging the ions according to their coagulating power the series becomes, ferrocyanide > ferricyanide > sulphate > phosphate > oxalate, ferrocyanide having the greatest coagulative power and the oxalate the least. It is evident from these results that ions having the greatest coagulating power are the least absorbed; thus the tetravalent ion ferrocyanide has a high coagulating power and at the same time is the least absorbed. These results further show marked variation from those obtained by Freundlich and Ishizaka (*loc. cit*). Weiser and Middleton commenting on results of Freundlich and Ishizaka point out that it is very unsafe to draw conclusion from adsorption data where the amount of adsorption is very small as has been obtained by Ishizaka with “grown” alumina (.002 to .055 millimole per gram). Further it may be remarked here that the adsorption values for colloidal aluminium hydroxide were determined above the precipitation concentration. Freundlich and Ishizaka themselves concluded that “smaller concentrations should have been used in the determination of these adsorption values such as were used in the determination of precipitation values”. It will be obvious from these considerations that the series obtained by Weiser and Middleton (*loc. cit.*) and by Freundlich and Ishizaka (*loc. cit.*) should differ materially as the adsorption values were determined under different concentration of the electrolytes and under different conditions.

It has already been stated that in our own experiments on the coagulation of manganese dioxide sol and on the adsorption of ions by precipitated manganese dioxide we have noticed that, in general, ions of higher valencies having greater coagulating powers are adsorbed less than the ions of lower valencies. It is now desirable to analyse the actual experimental results obtained by us in details especially as the data obtained by Weiser and his collaborators confirm the conclusions we have arrived at from our own experiments.

It may be noted here that, up to this time, almost all researches on direct adsorption by a solid adsorbent have been performed with charcoal; but it is well known that even if charcoal be prepared from one source its composition cannot be made constant. Thus cocoanut charcoal, which has been very largely used for adsorption experiments differs in composition and impurities according to the manner and source from which it is prepared. Even the temperature at which carbonisation is carried out has very great influence on the adsorptive power of charcoal. Again it is extremely difficult to get the substance with particles of uniform size, which condition is of primary importance in the surface phenomenon. Charcoal, therefore, appears to be not at all suited for the investigation of the problem with a view to the formulation of the laws of adsorption.

In the following table results of adsorption of some electrolytes by chemically pure and air-dried hydrated manganese dioxide are given. In all cases it has been observed that mainly the cations are adsorbed by the solid.

Electrolyte.	Strength of the solution.	Amount adsorbed in milliequivalent per gram MnO_2
$MnCl_2$	.5N	.618
$ZnSO_4$	.5 N	.854
$CuSO_4$	.5 N	1.463
$CuCl_2$	.48 N	.963
$Ni(NO_3)_2$	.5 N	.381
Potash alum	.48 N	.272
$Fe_2(SO_4)_3$	.46 N	.272
Th $(NO_3)_4$	.48 N	.581

Arranging the ions in order of their adsorbability and beginning with the one most absorbed, the following series is obtained:—

Cu > Zn > Mn > Th > Ni > Fe, Al. In another set of experiments the following series is obtained:—

Ag > Cu > Cd > Zn, Mg > Ba > Sr, Ca > Al.

In the following table results obtained by the adsorption of electrolytes by hydrated MnO_2 in course of precipitation are given:—

Electrolyte Conc = N/1	Amount adsorbed in Milliequivalents per gram MnO_2	Electrolyte. Conc = N/1	Amount adsorbed in Milliequivalents per gram MnO_2
$AgNO_3$	6.107	$ZnSO_4$	.431
NaCl	2.876	$Ni(NO_3)_2$	.503
LiCl	1.382	$FeCl_3$	1.234
$CdSO_4$	.800	Potash Alum	.082
$CuSO_4$	1.150	$UO_2(NO_3)_2$	.293
$BaCl_2$	.594	$Th(NO_3)_4$	.096

Examining the above table the order of the ions according to their adsorption becomes Ag > Na > Li > Cu > Cd > Ba > Ni, Zn > UO_2 > Th > Al.

It will be observed from these quantitative results that many ions of lower valency are more adsorbed than ions of higher valency. Thus the monovalent silver, sodium, and lithium ions are more adsorbed than any of the bivalent, trivalent, or tetravalent ions. Again the trivalent ion aluminium is far less adsorbed than most of the bivalent ions. These facts show that the ions of higher valency, which in general have greater coagulating powers are adsorbed the least. This conclusion arrived at from a careful scrutiny of the experimental results of different investigators as well as of our own is in direct opposition to the view hither to held, notably by Freundlich and Weiser. Bancroft in his article on precipitation and peptisation[1] has interpreted the Schulze-Hardy Law in a peculiar way. "While it is generally true that an ion of higher valence will be adsorbed more strongly than that of lower valence, this so-called law of Schulze-Hardy is only a first approximation, and should be considered only as a guide." Again on page 11 he says "Whilst there is unquestionably a tendency for ions of a higher valence to be adsorbed more strongly than ions of a lower valence, the experiments which have been cited show that there are many exceptions and that the fundamental rules is that adsorption is specific both as regards the adsorbing substance and the ion adsorbed". . . . The above view has been accepted by Lewis[2]. There are two statements in the above quotation which require some comment. From the experimental results already cited it is clear that there is absolutely no justification in holding the view that ions of higher valence are adsorbed to a greater extent than those of lower valence. On the contrary the results show that ions of lower valence are adsorbed more than those of higher valence, and it seems to us that the real explanation of the Schulze-Hardy Law rests in the recognition of this fact. Since the coagulation of an equal amount of a colloid by ions of different valencies, is at first an electrical phenomenon, it will be clear that for the electrical neutralisation of a fixed amount of any colloid the absolute amount of ions, expressed in gram molecules, necessary in the case of monovalent ions will be greater than that of di- or tri-valent ions, simply because the net charge on a di- or tri-valent ion is greater than that of a monovalent ion. It will be apparent, therefore, that for one purely electrical neutralisation by adsorption, the greater the coagulating power of an ion, the less will be its adsorption. In our opinion, therefore, up till now, the real significance of the Schulze-Hardy Law has not been clearly perceived.

The few apparent deviations from this rule can be easily explained. In the coagulation of a colloid there are two distinct steps in which adsorption occurs. The first step is the electrical neutralisation of the charge on the colloidal particles through adsorption of an ion carrying a charge opposite to that on the sol and only here the Schulze-Hardy Law is applicable. The adsorption, however, does not stop there, but the coagulated particles further act as an

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[1] Second B. A. Report on Colloid Chemistry, p.8, (1918).

[2] System of Physical Chemistry **1**, 348 (1921).

adsorbent, taking up an additional amount of the electrolyte or ion. The amount of this second adsorption will depend on the adsorbability of the electrolytes or ions and the nature of the coagulated mass concerned and hence the final amount of adsorption may have any value depending on the above factors. The Schulze-Hardy Law cannot be rigidly applied to these cases. If the adsorption by the neutral particles is not appreciable, then the Schulze-Hardy Law is likely to be followed; but if the neutral particles can adsorb the ion or the electrolyte appreciably, complications will arise and the Schulze-Hardy Law may not be applicable. The existence of these two steps in adsorption has been recognised by Weiser and his collaborators (*loc. cit.*) who have emphasised that in the determination of adsorption by a coagulating colloid the amount of adsorption by the agglomerated particles must be taken account of. It will thus be observed that the interpretation of the Schulze-Hardy Law advanced in this paper is in agreement with experimental results, and it explains in a consistent manner the fact that in majority of cases an ion with the greatest coagulating power is least adsorbed.

Bancroft (*loc. cit.*) has stated that ions of higher valency are adsorbed "more strongly" than ions of lower valency. We are not aware of any direct experiment in which the attractive force by which an adsorbed ion is retained by the coagulated mass has been determined. Moreover the adsorption process is practically instantaneous in the majority of cases investigated. Linder and Picton[1] have shown that when arsenious sulphide is precipitated by barium chloride or strontium chloride, only a small portion of the metallic radical is adsorbed by the coagulated sulphide. If the precipitate containing the adsorbed salt is shaken with potassium or sodium chloride, the adsorbed metal is displaced by sodium or potassium and comes out in the solution which can be tested. This shows that the bivalent barium is not adsorbed more strongly than the univalent potassium or sodium and this is contrary to Bancroft's view. We have found that hydrated manganese dioxide containing some adsorbed copper or any other metal loses the metal when shaken with potassium or sodium chloride or with the aqueous solution of any other electrolyte. This phenomenon is of general occurrence. These results indicate that in the present state of our knowledge of the phenomenon of adsorption, we cannot say with precision whether one ion is adsorbed "more strongly" than another, when the adsorption is of the same type.

It may be of interest at this stage to consider the question of minimal concentration of an electrolyte necessary to coagulate a sol. It is well known that a certain minimum concentration of electrolyte is necessary to coagulate a given amount of a colloid, though a small percentage of the added electrolyte at the minimal concentration is actually used up in coagulating the sol, the major portion of the electrolyte remains unadsorbed. No satisfactory explanation of this fact has yet been given. It is certainly interesting that a minimum concentration of an electrolyte would be necessary for the precipitation of a colloid, when the actual amount required for the coagulation is far less than the so-called minimal concentration. In order to understand this process it is necessary to take recourse to certain kinetic consideration.

It is well known that in explaining the finite velocity of ordinary chemical reactions in homogeneous medium it is assumed that all the molecules of the reacting substances are not in the same state of reactivity. At any instant, only a very small portion of them are reactive, and these active molecules or ions determine the velocity of the particular reaction at a certain temperature[1] We can conceive therefore, that all the ions from an added electrolyte and carrying a charge opposite to that on the sol are not in the same state of activation, and that only the active ions can be adsorbed by the sol and are capable of precipitating it. Hence a minimal concentration of an electrolyte means that concentration where the amount of active and consequently of adsorbable ions is just sufficient to precipitate the sol. In order, therefore, to explain the experimental results on adsorption we have to assume that only a few percents of the ions carrying a charge opposite to that of the sol are active as far as precipitation of the sol is concerned and that the active portion of the ions is adsorbed by the solin course of its precipitation.

It is an experimental fact that with the same weight of a solid adsorbent, the greater the concentration of the solute, the greater is the adsorption. On the addition of a small amount of an electrolyte to a sol, only a certain percentage of the ion carrying a charge opposite to that of the sol will be adsorbed by the colloidal particles depending on the concentration of the added electrolyte. If the particles of the sol are of uniform size, fractional precipitation of the sol is not likely to occur, because the uncharged colloidal particles carrying the adsorbed material may come in contact with the neighbouring charged particles and are likely to form bigger particles in combination with the charged particles. Because of their charge and of their Brownian movement, these bigger particles, though now more unstable, will still remain in suspension. Hence the presence of charged particles is likely to exert a peptising influence on the neighbouring uncharged ones. Gradually the concentration of the added electrolyte is increased and with it the amount of adsorption of the precipitating ion is also increased. At the minimal concentration, that much of the precipitating ion is adsorbed which is required for the complete neutralisation of the electric charge on the colloid particles.

There are some apparent deviations from the simple case discussed where the particles of the sol are assumed to be of uniform size. In the case of colloidal sulphur, mastic, etc., fractional precipitation by electrolytes is possible, because all the particles in the sols are not of the same size and consequently of the same degree of stability. Thus Oden[2] obtained particles of different size on fractional precipitation of a sulphur sol. Moreover, Murray[3] has obtained particles of mastic of different sizes by fractional precipitation of a sol by means of hydrochloric acid. These facts show that in the colloidal solu-

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[1] Cf. Dhar: J. Chem. Soc. 111, 745 (1917).

[2] Kolloid-Z. 8, 186 (1911).

[3] Phil Mag. August, 401 (1922).

tions of these substances, particles of different sizes are present. From our experiments on the adsorption of sols with precipitated $BaSO_4$, we have observed that the larger the particle the less is its stability and sols containing large particles are readily adsorbed and precipitated by $Ba\ SO_4$. Hence fractional precipitation of a sol on the addition of an electrolyte is likely to take place in those cases where the particles of the sol are not of uniform size and consequently of different degrees of stability.

From a critical survey of our own experiments as well as of the existing data on the effect of concentration of a sol on its coagulation by electrolytes, we have shown in the foregoing paper of this series that the greater the concentration of a colloid, the greater would be the amount of an electrolyte necessary to coagulate it, irrespective of the valency of the precipitating ion. This generalisation is also supported by the experimental work of Weiser and Nicholas[1]. It is also well known that emulsions behave like sols in most respects. Hence it is very likely that this simple rule regarding the effect of concentration of a sol on the coagulating power of an electrolyte should also hold in the case of emulsions.[2]

Charge Reversal of Colloids

In the foregoing paper[3] of this series it has been shown that freshly precipitated ferric hydroxide when shaken with the solution of arsenious acid passes into a negatively charged colloid. In the same paper it has also been observed that in presence of protecting substances like glycerol, cane sugar, grape sugar, etc., ferric hydroxide, cobalt hydroxide, cupric hydroxide etc., can be peptised and can be made to take up negative charge. By the gradual addition of an alkali to a mixture of ferric chloride and glycerol or sugar there are three definite stages through which the colloid passes—first it becomes positively charged, then coagulation occurs on neutralisation of the change and finally it passes into a negatively charged colloid. This order can be changed by the addition of suitable electrolytes.

In another part of this series of papers it has been observed that freshly precipitated ferric hydroxide passes into a negatively charged sol when shaken with aqueous solutions of sodium arsenite, sodium oxalate, sodium tartrate, sodium citrate etc.

Recently we have observed that when ferric hydroxide is precipitated in the cold by mixing ferric chloride and ammonium hydroxide and washed with distilled water till the filtrate is free from chloride, the ferric hydroxide can pass as a negatively charged sol due to the adsorption of OH′ ions from ammonium hydroxide. In other words ferric hydroxide can very readily pass into a negatively charged colloid. Moreover, it is well known that in the ordinary methods of preparing the sol we get a positively charged colloid. These facts immediately point to the influence of the medium on the nature of

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[1] J. Phys. Chem. 25, 742 (1921).

[2] Compare, however, Bhatnagar: J. Phys. Chem. 25, 735 (1921).

[3] Kolloid-Z. (1923).

the electrical charge carried by the colloidal particles. The presence or absence of certain kinds of ions in the medium accounts for the nature of the electric charge on the particles of the sol. In a foregoing paper[1] we have emphasised the view that the amount of adsorption of an ion by an adsorbent is a fundamental factor in charge reversal. Valency of the ion in question is only important when it implies the amount of charge on an ion, because in order to have reversal of charge the colloid needs adsorb only a small amount of ions of higher valency in comparison with ions of lower valency. Hence if the amount of adsorption is great, a monovalent ion can reverse the charge on a colloid. Thus hydrochloric acid has been found to reverse the charge on antimony sulphide sol, similarly sodium hydroxide or potassium hydroxide can reverse the charge of ferric hydroxide peptised by sugar or glycerol.

It has already been stated that freshly precipitated hydrated manganese dioxide can adsorb a large amount of silver ions from silver nitrate. It has now been observed that monovalent silver ions can reverse the charge on colloidal manganese dioxide, consequently it is apparent that those sols which are likely to adsorb markedly monovalent ions like $Ag^{\cdot}$, $Hg^{\cdot}$ (ous), should undergo charge reversal in the presence of these ions. We have repeatedly observed that freshly precipitated ferric hydroxide is a very good adsorbent and it has been found out that it adsorbs both acids and alkalies. From equivalent concentrations the amount of adsorption for an acid is much greater than that for an alkali, because $Fe(OH)_3$ is more basic than acidic. It has also been found that it markedly adsorbs mainly the acidic portion from the solutions of salts like sodium oxalate, sodium arsenite, sodium phosphate, sodium citrate, sodium tartrate, etc., and that it is impossible to free ferric hydroxide from these substances even by repeated washing and it has been conclusively shown that these electrolytes charge freshly precipitated ferric hydroxide negatively. It is also well known that these salts form complexes with ferric ion. It is certain, therefore, that a neutral substance like ferric hydroxide can pass into a positively or negatively charged sol according to the amount of adsorption of a positive or a negative ion. Recently Weiser[2] has shown that freshly precipitated cupric hydroxide when shaken with solutions of KCl, NaCl, adsorbs the acid portion leaving the filtrates alkaline.

In this connection it is of interest to note that those substances which can form complex salts with the adsorbent are likely to be adsorbed most. Thus Ishizaka (*loc. cit.*) has shown that potassium salicylate, potassium ferrocyanide and potassium oxalate are adsorbed most by a sol of aluminium hydroxide. Similar results are obtainable with ferric, hydroxide. Evidently the phenomenon of adsorption is most marked when there is some sort of chemical affinity between the adsorbent and the substance which is being adsorbed.

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[1] J. Phys. Chem. 27, 376 (1923).

[2] J. Phys. Chem. 27, 501 (1923).

We have already proved[1] that hydrated manganese dioxide is a good adsorbent and it has been found that it adsorbs mainly the basic portion from salt solutions and very small portion of the negative part is adsorbed. It also adsorbs both hydrogen and hydroxyl ions and from the following results it will be seen that for equivalent concentrations the hydroxyl ions are more adsorbed than hydrogen ions.

Solution used.	Amount of $H^{\cdot}$ or OH' present originally	Amount of $H^{\cdot}$ or oH' adsorbed.
Sulphuric acid.	.0094 gr. of $H^{\cdot}$	.0003 gr. of $H^{\cdot}$
Acetic acid.	.0162 gr. of $H^{\cdot}$	.0003 gr. of $H^{\cdot}$
Sodium hydroxide.	.017 gr. of OH'	.008 gr. of OH'
Sodium hydroxide.	.034 gr. of OH'	.011 gr. of OH'
Potassium hydroxide.	.017 gr. of OH'	.008 gr. of OH'
Potassium hydroxide.	.034 gr. of OH'	.011 gr. of OH'

It appears, therefore, that hydrated manganese dioxide which behaves like manganic acid H_2MnO_3, and is also acid to litmus, can adsorb large quantities of OH' ions because an acidic substance naturally has a great affinity for OH' ions. Incidentally we should like to mention that our experimental results carried on with chemically pure absorbents are in entire disagreement with the views expressed by Oden and Andersson[2] on the nature of the decomposition of an electrolyte by adsorption. It is evident that a neutral substance having a large surface will adsorb gases and liquids and that is why substances are copiously adsorbed by charcoal. When solutions of electrolytes are shaken with charcoal, both the acid and basic portions are adsorbed and consequently no question of change of electric condition of the adsorbent arises. If there is some sort of chemical affinity between charcoal and the substance which is being adsorbed, the result will be more marked. In Weiser and Sherrick's experiments (*loc. cit.*) on the adsorption of substances by $BaSO_4$ in the course of precipitation it is found that those ions which form sparingly soluble barium salts are adsorbed most, because sparingly soluble salts are more allied to barium sulphate.

We have observed that pure silica, when carefully washed with hydrochloric acid and freed from the acid by repeated washing, is shaken with salt solutions like $CuSo_4$, $NiCl_2$, alum, etc., can adsorb the basic portion from these salt solutions. The adsorbed substance cannot be removed by washing. We have also observed that the basic portion adsorbed by hydrated manganese dioxide from substances like $Bacl_2$, $CuSO_4$, $NiCl_2$, alum, $AgNO_3$, etc., cannot be removed by washing, whilst the basic portion adsorbed by hydrated MnO_2 from NaCl, KCl, etc., can be slowly but completely removed by washing. Consequently the adsorption of basic portion of substances like $CuSO_4$, $NiCl_2$, etc., is more or less permanent, and hence many authors call these

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[1] Chatterji and Dhar: *loc. cit.*

[2] J. Phys. Chem. 25, 322 (1921).

substances manganites of the corresponding metals[1]. Exactly similar results are obtained with hydrated silica, the basic portion adsorbed from NaCl, KCl, etc., can be slowly but completely removed by washing, whilst the basic portion adsorbed from $CuSo_4$, alum, etc., cannot be removed by washing. Just as manganese dioxide is capable of adsorbing both acids and bases, similarly silica can also adsorb both acids and bases and a base is more adsorbed than an acid, because silica is acidic in nature. The amount of adsorption of acids by silica is very small and is only a few per cent of the total quantity of the acid taken. This adsorption is more or less due to the surface effect and is allied to the adsorption of substances by charcoal, but the adsorption of bases by silica is connected with chemical affinity and is more permanent.

It is well known that silicic acid can remain peptised in presence of both $H^{\cdot}$ and OH' ions. In presence of $H^{\cdot}$ ions, it remains positively charged, whilst in presence of OH' ions it is negatively charged. The uncharged substances like silicic acid, hydrated MnO_2, $Fe(OH)_3$, etc., can pass into a positive or a negatively charged sol due to the adsorption of $H^{\cdot}$ ions or OH' ions according to circumstances.

From the foregoing results it is apparent that charge reversal will depend a great deal on the amount of adsorption as well as on the permanency of adsorption. Those substances which are markedly adsorbed and which cannot be removed by washing are more active in charge reversal than those which are not adsorbed in large quantities and are removable by washing.

From our own experiments we have observed that negatively charged ferric hydroxide sol can be obtained by arsenite ion, oxalate ion, tartrate ion, etc., which are markedly and permanently adsorbed by ferric hydroxide. Similarly charge reversal has been observed with hydrated manganese dioxide by even the monovalent $Ag^{\cdot}$ ion which is markedly and adsorbed by hydrated manganese dioxide. From our experiments we find that hydrogen ions and hydroxyl ions are appreciably adsorbed by freshly precipitated ferric hydroxide, at the same time charge reversal can be readily effected by these two univalent substances. It is very likely that $H^{\cdot}$ ions will be adsorbed appreciably by sulphides of arsenic, antimony, etc., and that is why charge reversal of these substances is possible with the help of $H^{\cdot}$ ions.

Recently Mukherji[2] has stated that silica can adsorb acetic acid, citric acid, salicylic acid, hydrochloric acid, etc., This fact has been contradicted by Joseph and Hancock[3]. We have observed that hydrated MnO_2 can adsorb acetic acid and other acids; similarly we have found that silica adsorbs acetic acid and other acids to a slight extent. This kind of adsorption of substances by uncharged adsorbents like charcoal, silica, hydrated MnO_2, etc., is mainly a surface effect and is insignificant in comparison with the adsorption due to the chemical affinity between the adsorbent and the adsorbing substance, as

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[1] Cf. Sarkar and Dhar: Z. anorg. Chem. 121, 135 (1922).

[2] Phil. Mag. 6, 44, 343 (1922); Nature 110, 732 (1922).

[3] J. Chem. Soc. 123, 2022 (1923).

has already been said that silica will adsorb bases in greater amount than acids. Very recently Glixelli[1] has observed an augmentation of the acidity of silica gels under the influence of a neutral salt. The effect can be readily explained by the adsorption of NaOH by the silica particles, setting free hydrochloric acid.

In view of the above facts the phenomenon of soil acidity can be very readily explained. We know that soil contains silica as well as humic acid. These two substances will certainly adsorb the basic portion from neutral salts present in the soil setting free acid and thus making the soil acid. The adsorbed basic portion might form unstable adsorption compounds of the type of the so-called manganites which are sparingly soluble. It is well known that sodium salts of pyroantimonic acid, dihydroxy tartraric acid, complex silicic acid, etc., are very sparingly soluble. It is very likely that the adsorption compounds obtained from humic and silicic acids would be sparingly soluble. Moreover, it has been noted in the foregoing pages that the basic portion adsorbed by MnO_2, SiO_2, etc., from such salts as NaCl, KCl, etc., are very slowly removed by repeated washing. Hence from the foregoing experimental results it appears that soil acidity is most likely due to the adsorption of basic portions of salts by silica, humic acid, etc., present in the soil. We are, therefore, unable to support the view on soil acidity expressed by Oden[2] which rests on the assumption that humic acid adsorbs the inorganic and organic acids already present in the soil.

It must be emphasised that substances like $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, As_2S_3, Hgs, CuS, SnO_2, S, SiO_2, etc., which are neither strongly acidic nor basic can adsorb either $H^{\cdot}$ or OH' ions and pass into positively or negatively charged sol and hence the formation of colloids and charge reversal with these substances are comparatively easy.

It is now easy to explain the charge reversal of a colloid simply from the adsorption point of view. The first step in the formation of a colloid is the preferential adsorption of one ion which peptises the substance and gives the necessary charge to the otherwise uncharged substance, for the stability of the sol. If we now add an electrolyte, the charge on the colloidal particles will be neutralised by the oppositely charged ions. Two things might happen at this stage. If the particles of the neutral substance cannot adsorb more of the precipitating ion it will coalesce and finally coagulate. If, on the other hand, the neutral substance is capable of adsorbing more of the precipitating ion immediately, it will be converted into the oppositely charged sol and consequently charge reversal will take place. Evidently charge reversal will depend a great deal on the amount and permanency of adsorption of the precipitating ion by the neutral substance obtained by the coagulation of the colloid.

Linder and Picton (*loc. cit.*) have proved that when arsenious sulphide is precipitated by $BaCl_2$ or $SrCl_2$ the metallic radical is adsorbed by the coagulated sulphide. The above authors have observed that the adsorbed ions

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[1] Compt. rend. 176, 1714 (1923).

[2] Trans. Faraday Soc. 17, 292 (1922).

cannot be removed by washing. We repeated the above experiments with sols of As_2S_3 and Sb_2S_3 and we have obtained results contrary to the observations of the foregoing authors. We have been successful in completely removing Ba or Sr from the coagulated sulphides by repeated washing with water. Linder and Picton have also shown that the coagulated sulphides containing Ba or Sr when shaken with excess of K or Na salts give out the Ba or Sr Salt in solution and this can be tested. This has been recently contradicted by Charriou[1]; but we have found that the observation of Linder and Picton is quite correct and that excess of sodium or potassium salt can drive out Ba or Sr ions from their adsorbed condition. This happens because the adsorption of these substances is practically of the same order, and since, the univalent ions are used in large excess, the effect of mass will predominate. Charriou has also shown that chromic acid adsorbed by $Al(OH)_3$ cannot be driven out by chlorides, nitrates or acetates of alkali metals but it can be displaced by oxalates, sulphates, phosphates, etc. These results can be very readily explained from the work of Weiser and Middleton (*loc. cit.*) on the adsorption of the foregoing ions by $Al(OH)_3$. Weiser and Middleton have shown that dichromate ion is highly adsorbed and hence the displacement will depend on the amount of adsorption and concentration of the displacing electrolyte. If the displacing electrolyte is only slightly adsorbed by $Al(OH)_3$, then chromic acid will not be displaced even by concentrated solutions of the displacing electrolyte.

It should be emphasised that the amount of adsorption by a definite weight of adsorbent would be directly proportional to the molecular weight of the substance in question under otherwise similar conditions. It has already been shown that the amount of adsorption of electrolytes by freshly precipitated manganese dioxide increases with the increase in their atomic weights when the elements occur in the same periodic table.[2] Similar results have been obtained by Oden and Andersson[3] in the adsorption of alkali and alkaline earth metals by charcoal. In the adsorption of anions, Oden and Langelius (*loc. cit.* p. 385) have shown that, in general, amongst ions having the same valency, the greater the molecular weight the greater is the adsorption. Moreover, it has been observed that the bigger the particles in a medium, the greater is the adsorption by an adsorbent.

From our experiments on adsorption we find that substances like freshly precipitated $Fe(OH)_3$, hydrated MnO_2, etc., have marked adsorptive power and are in certain respects comparable to charcoal, whilst substances like As_2S_3, Sb_2S_3, $BaSO_4$, etc., have very slight adsorptive power, though all these substances can adsorb appreciably electrolytes in the course of their formation. Consequently the uncharged substances like As_2S_3, Sb_2S_3, etc., cannot adsorb the precipitating ions to any appreciable amount. Hence the amount of different ions adsorbed by As_2S_3, Sb_2S_3, etc., in the process of

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[1] Compt. rend., 176 1890 (1923).

[2] Ganguly and Dhar: J. Phys. Chem. 26, 836 (1922).

[3] J. Phys. Chem. 25, 311 (1921).

coagulation is more or less equivalent as was shown by Whitney and Ober (*loc. cit.*) and Freundlich (*loc. cit.*). On the other hand, the neutralised substances like hydrated MnO_2, $Fe(OH)_3$, etc., are capable of adsorbing appreciably the precipitating ions; hence in these cases the amount of ions adsorbed by a coagulating sol is bound to be different and are not in equivalent proportion.

From the discussions and our researches in this line we are of the opinion that charge reversal, amount of adsorption and complex formation go hand in hand and depend upon the chemical affinity existing between the adsorbent and the substance which is being adsorbed.

Experiments on adsorption and reversal of charge in various directions are in progress in these laboratories.

Summary

(1) From a survey of the experimental results on coagulation and adsorption it is found that an ion which has a high precipitation value (a small coagulating power) for a colloid is most adsorbed by the colloid. Inversely the smaller the precipitation value (that is, the greater the coagulating power), the less is the adsorption. This is the proper explanation of the so-called Schulze-Hardy Law. The above generalisation is supported by the actual experimental results of various workers.

(2) On the addition of an electrolyte to a sol the first step is the neutralisation of the electric charge on the colloid particles, by the adsorption of ions carrying a charge opposite to that of the sol. The second step is the further adsorption of the electrolyte by the neutral particles. It is only for the first step that the Schulze-Hardy Law is applicable.

(3) A suggestion based on kinetic and adsorption points of view, explaining the existence of a minimal concentration of electrolytes for the coagulation of colloids, has been advanced.

(4) Charge reversal depends essentially on the amount as well as on the permanency of adsorption. Ions such as hydrogen, hydroxyl, etc., which are more or less permanently adsorbed in large quantites are most active in charge reversal.

(5) Substances which are neither strongly acidic nor strongly basic, are capable of adsorbing positive or negative ions and pass into the colloidal state. Charge reversal with these cases are also very frequent.

(6) It appears that charge reversal is possible in those colloids where the neutralised particles of the sol can immediately adsorb more of the precipitating ion.

(7) We are of opinion that charge reversal, amount of adsorption and complex formation go hand in hand and depend on the chemical affinity existing between the adsorbent and the substance which is being adsorbed.

(8) Recent experimental work on the adsorption of the basic portion from salt solutions by silica, cupric hydroxide, manganese dioxide, etc., proves that soil acidity is very likely due to the adsorption of basic portion from salts by silica, humic acid, etc., present in the soil.

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ACTION OF METALS ON NITRIC ACID

BY WILDER D. BANCROFT

For nearly thirty years I have carried the reduction of nitric acid by metals in my notebooks as a major problem to be taken up as soon as possible, and at different times during that period I have suggested it to graduate students as a desirable thesis subject—all in vain. Three years ago I found in Mr. L. H. Milligan a student who was both competent to tackle the problem and interested in it. Rather to my dismay it turned out that the methods of analysis were not satisfactory and consequently Mr. Milligan's thesis, which will be published soon, had to be on analytical methods and not on the real problem at all. Fortunately he was able to do enough additional work to make it seem certain that the underlying theory was sound and that the problem now is primarily one of collecting data. Since it may be many years before we get the whole question cleaned up and since we would like very much to get other laboratories interested in the subject, it has seemed worth while to present a general outline of the situation as we now see it and to follow this up with the experimental papers as fast as we can get them finished. Some day it is to be hoped that the general theory of the reduction of nitric acid will be worked out as clearly and definitely as is the theory of the reduction of nitrobenzene.

There are two quite distinct problems in the reduction of nitric acid: the question of the intermediate stages; and the part played by any given metal. The solving of the second problem carries with it the solving of the first.

Acworth and Armstrong[1] believe that the direct reduction products are nitrous acid, hyponitrous acid, hydroxylamine, and ammonia, with nitrogen peroxide, nitric oxide, nitrous oxide, and nitrogen as secondary products. Ostwald[2] believes that the reduction of nitric acid starts from a dissociation into $NO_2^{\cdot}+OH'$ and that consequently the direct reduction products are nitrogen peroxide, nitrous acid, nitric oxide, hyponitrous acid, and either nitrogen or hydroxylamine and ammonia; with nitrous oxide presumably a dehydration product of hyponitrous acid. The same view is taken by the unknown author (presumably Partington) in Thorpe's Dictionary of Applied Chemistry, 4, 561 (1922).

Mellor[3] is distinctly non-committal; but rather inclines to Ostwald's view. "Some consider that the first product of the reaction is a nitrate of the metal and nascent hydrogen: $Cu+2HNO_3=Cu(NO_3)_2+2H$. The nascent hydrogen is then supposed to reduce the nitric acid to nitrous acid. With some metals, the reduction of the nitric acid proceeds much further, say through the stages: $NO_2\longrightarrow HNO_2\longrightarrow NO\longrightarrow N_2O\longrightarrow N_2\longrightarrow NH_3$. Free hydrogen is seldom evolved because it is so rapidly oxidized by the nitric acid. However,

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[1] J. Chem. Soc. 32, 56 (1877).

[2] Grundriss allg. Chemie, 440 (1899).

[3] "Modern Inorganic Chemistry", 514 (1912).

free hydrogen is said to have been obtained by the action of nitric acid on manganese and on magnesium. The reducing actions indicated above can be represented[1] symbolically:

$$\begin{array}{ll} 2HNO_3+2H=2H_2O+2NO_2 & 2HNO_3+8H=5H_2O+N_2O \\ 2HNO_3+4H=2H_2O+2\,HNO_2 & 2HNO_3+10H=6\,H_2O+N_2 \\ 2HNO_3+6H=4H_2O+2NO & 2HNO_3+16H=6H_2O+2NH_3 \end{array}$$

Some believe that the acid first oxidizes the metal[2] to the oxide, *e.g.* $3\,Cu+2HNO_3=3CuO+H_2O+2NO$; and that the oxide then dissolves in the acid to form the nitrate: $CuO+2HNO_3=Cu(NO_3)_2+H_2O$. *When differences of opinion can reasonably be entertained, it follows that our knowledge of the facts is incomplete, and that more experimental work is needed.* The metals copper, silver, mercury, and bismuth have no perceptible action on cold dilute sulphuric and hydrochloric acids, and accordingly it is not likely that they will reduce nitric acid by the action of nascent hydrogen. V. H. Veley (1890) proved that these metals have no action on cold dilute nitric acid unless a trace of nitrous acid or a lower nitrogen oxide is present. Nitrous acid may be present in the nitric acid as an impurity; it may be formed by the incipient decomposition of nitric acid when it is warmed; or it may be formed in the acid by electrolysis produced by local currents of electricity set up by impurities in the metal ('local action'). Once the action has started, the evolution of nitric oxide, and the formation of nitrate proceeds quickly. According to Veley, therefore, the dissolution of this metal in nitric acid proceeds: $Cu+3HNO_3+HNO_2+H_2O$, is the resultant of a series of consecutive reactions: $Cu+4HNO_2=Cu(NO_2)_2+2H_2O+2NO$; followed by $Cu(NO_2)_2+2HNO_3=Cu(NO_3)_2+2HNO_2$; the small trace of nitrous acid thus acts as a catalytic agent; nitrous acid is continuously produced and continuously decomposed: $3HNO_2=HNO_3+2NO+H_2O$."

Roscoe and Schorlemmer[3] dodge the whole question. "As already mentioned, nitric acid dissolves a large number of metals with formation of nitrates. Hydrogen is not evolved at the same time, as is the case with sulphuric and hydrochloric acids, but in its place lower oxides of nitrogen and even nitrogen itself and ammonia are formed. The explanation frequently given of this change is that hydrogen is first produced, but that it at once acts on the excess of nitric acid present, forming water and the lower oxides of nitrogen. Thus, for example, the formation of nitric oxide by the action of copper on nitric acid is supposed to take place in the two following stages:—

$$Cu+2HNO_3=Cu(NO_3)_2+2H$$
$$6H+2HNO_3=2NO+4H_2O.$$

"According to Veley,[4] however, this explanation is not correct, inasmuch as pure copper, mercury, and bismuth do not dissolve in pure dilute nitric acid,

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[1] Cf. Montemartini: Gazz. chim. ital. **22**, I, 339 (1892).

[2] This is the view held at one time by Higley: Am. Chem. J. **17**, 26 (1895). It is still taught at Harvard.

[3] "A Treatise on Chemistry", **1**, 544 (1920).

[4] Proc Roy. Soc. **46**, 216 (1890); **52**, 27 (1893); Phil Trans. **182 A**, 312 (1891); J. Soc. Chem. Ind. **10**, 204 (1891).

but dissolve readily when nitrous acid is present the change at any moment being directly proportional to the mass of the nitrous acid in the solution, and the more rapid the greater the proportion of the former to the latter. He therefore believes that the reaction is started either by traces of nitrous acid already present or by impurities in the metal inducing a local electric current; the first product of the reduction of the metal is nitrous acid, and the production of lower oxides of nitrogen he regards as due to the subsequent changes occurring between nitrous acid and the metallic nitrate or nitrite in presence of an excess of nitric acid, the nitrous acid being decomposed as fast as it is formed.

"The relative proportion of the products formed varies not only with the concentration of the acid and the temperature, but also with the nature of the metal employed. Thus silver when treated with acids of sp. gr. 1.05-1.4 yields nitric oxide and nitrogen peroxide, but no nitrous oxide, whereas lead with an acid of sp. gr. 1.2 yields a gas of which forty percent is nitrous oxide."

Norris[1] states explicitly that the first action of nitric acid on metals is an oxidizing one. The square brackets indicate substances which are not actually set free as such. "Nitric acid oxidizes all the metals except the so-called noble metals, gold and platinum, for example. The nitrates formed are soluble in water and, consequently, nitric acid dissolves these metals. . . . In writing equations for the reactions involved, it is best to separate them into steps and combine the partial equations in the way already explained. For example, the oxidation of copper by nitric acid can be represented as follows:

$$2HNO_3 = 2NO + H_2O + [3O]$$

$$3\,Cu + [3O] = [3CuO]$$

$$[3CuO] + 6HNO_3 = 3Cu(NO_3)_2 + 3H_2O$$

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO."$$

Howe[2] takes an intermediate viewpoint. He says that "the reaction between zinc and nitric acid may be looked upon as taking place in two stages:

$$3Zn + 6HNO_3 = 3Zn(NO_3)_2 + 6H$$

$$6H + 2HNO_3 = 4\,H_2O + 2NO,$$

or, summing up these reactions:

$$3Zn + 8\,NHO_3 = 3Zn(NO_3)_2 + 4H_2O + 2\,NO.$$

It is perhaps better to look at this reaction from the standpoint of the oxidation of the metal, in which case we have the two equations:

$$3Zn + 2HNO_3 = 3ZnO + H_2O + 2\,NO$$

$$3ZnO + 6HNO_3 = 3Zn(NO_3)_2 + 3H_2O$$

which, when summed up, become as above:

$$3Zn + 8HNO_3 = 3Zn(NO_3)_2 + 4H_2O + 2NO."$$

This is playing safe with a vengeance. Unfortunately, as we shall see later, neither set of equations represents the facts.

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[1] "A Textbook of Inorganic Chemistry for Colleges," 327 (1921).

[2] "Inorganic Chemistry for Schools and Colleges," 270 (1920).

A great deal of work has been done on the reduction of nitric acid by metals with very little in the way of theoretical results. When this sort of thing happens over a period of years, it is usually safe to assume that the problem has been attacked from the wrong point of view. On looking over the literature it is easy enough to see where people have gone wrong. There has been the tacit assumption that the action of the metal depends on a single factor, whereas I shall show that we must consider not less than three factors, which do not necessarily run parallel as we change from one metal to another.

Acworth and Armstrong[1] say that "we regard the action of the metal as consisting simply in the displacement of the hydrogen of the acid and the formation of the corresponding nitrate in the manner expressed by the following equation, in which R denotes the amount of metal which is equivalent in combining or displacing power to two atoms of hydrogen:

$$R+2HNO_3=R(NO_3)_2+2H.$$

Under no circumstances, however, is the hydrogen thus displaced evolved as such; it at once acts on the free acid present (and even, in some cases, as we shall show later on, also on the metallic nitrate which has been formed), reducing it more or less completely to nitrous acid, nitrosidic acid [hyponitrous acid], hydroxylamine, or ammonia."

This is, of course, a special statement of the electrolytic theory of corrosion, long before it was developed as a general theory by Whitney[2] in 1903. A few years later I pointed out[3] that "the most striking characteristic of an electrolytic action is that it occurs in two places—at the anode and at the cathode. This peculiarity can be made less marked by bringing the electrodes nearer and nearer together. When the distance between them vanishes, we have a chemical reaction in the ordinary sense of the word and not an electrochemical reaction. Any chemical reaction, therefore, which can be made to take place electrolytically, must consist of an anode and a cathode process.[4] Considering the matter in this light, we see that there is a possibility of the anode and cathode processes interfering and of one perhaps masking the other.

"In some cases it is easy enough to tell what the anode and the cathode processes are. If we dissolve zinc in sulphuric acid, the formation of zinc sulphate is the anode process and the evolution of hydrogen is the cathode process. Now we know that pure zinc does not dissolve readily in sulphuric acid. Consequently we should expect to find a difficulty of some sort if we electrolyze sulphuric acid between the electrodes. We find this in the form of the so-called 'excess voltage' at the cathode; and in the electrolytic process we can obtain a more or less quantitative measurement of the phenomenon though we are still far from knowing the cause of it.

"A less simple case is that of copper in dilute nitric acid. Copper reacts chemically with dilute nitric acid, setting free nitric oxide. The formation of

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[1] J. Chem. Soc. 32, 56 (1877).

[2] J. Am. Chem. Soc. 25, 394 (1903).

[3] Trans. Am. Electrochem. Soc. 9, 13 (1906).

[4] Cf. Traube: Ber. 26, 1473 (1893); Haber: Z. physik. Chem. 34, 514 (1900).

copper nitrate must be the anode process and the reduction of the nitric acid the cathode process. When we start to test this we find difficulties. Everybody knows that we get ammonia instead of nitric oxide if we electrolyze dilute nitric acid, using a copper cathode. We have here an apparent contradiction, the chemical reduction yielding nitric oxide and the electrochemical one ammonia. Mr. Turrentine was good enough to solve the mystery for me. When copper reacts chemically with nitric acid, the anode product, copper nitrate, is formed at the same spot that the reduction takes place. In the electrolytic reduction of nitric acid with a copper cathode, the reduction takes place in a solution practically free from copper salt. The conditions are therefore not the same in the two cases. Mr. Turrentine therefore electrolyzed a solution of nitric acid and copper nitrate using a copper cathode. A gas was evolved at the cathode which proved on analysis to be chiefly nitric oxide. This experiment can be done in another form which is more striking. If dilute nitric acid be electrolyzed between copper electrodes, there will at first be no evolution of gas at the cathode. Gas will begin to appear as soon as the blue solution formed at the anode comes in contact with the cathode. A corollary to this is that ammonia would be formed in the chemical reaction between copper and nitric acid if the concentration of the copper salt could be kept sufficiently low. There did not seem to be any salt which one could add to the solution without introducing more complications than were eliminated. The difficulty was overcome by Mr. Turrentine in a distinctly ingenious manner. Strips of copper were hung vertically in a tall vessel. The copper nitrate flowed to the bottom of the vessel and the copper was removed by electrolytic precipitation in the form of cupric hydroxide. No current flowed through the copper strips and there was no copper cathode; but ammonia was formed.

"These experiments were performed to prove that the difference between the electrochemical and the chemical corrosion of copper by nitric acid was an apparent one only and due to an unsuspected difference in the conditions. In addition they illustrate the superior flexibility of the electrochemical method over the chemical method. In the electrochemical method there is no difficulty in varying the concentration of the copper salt at the cathode between any desired limits, while this is very difficult to do in the case of the chemical method. This is in addition to the advantage, which the electrochemical method always has, of permitting a wide variation in the rate of reaction for constant temperature and constant concentration. If we are ever to have a thorough knowledge of the chemical reactions between nitric acid and the metals we must study the problem electrochemically."

On the assumption that all corrosion is electrolytic in nature, it is evident that at least three independent factors must be taken into account in the reduction of nitric acid by a metal: the specific reducing power of the metal which may be measured by the hydrogen over-voltage in a corresponding sulphuric acid solution; the catalytic action of the metal on the various reduction products; and the catalytic action of the metallic nitrate on the various reduction products. This analysis of the problem is of no value unless we can devise methods of distinguishing the effects due to these three causes. Fortunately that is a very simple matter. We can determine the reduction products on adding different, dissolved, reducing agents having no catalytic action, which will give us the reduction products due to different electromotive forces. Of course it is possible that any given reducing agent may exert a catalytic action itself or through one of its oxidation products, and at least one case of this sort has already been found by Mr. Milligan. The catalytic action can be recognized and eliminated by using other reducing agents of about the same reducing power or by adding the same reducing agent to solutions of the different reduction products of nitric acid. This last method will be effective only in case the catalytic action is on one of the first reduction products of nitric acid, such as nitrous acid. There is no reason at present to suppose that there will be any special difficulty in distinguishing between reducing action and catalytic action.

Electrolysis of a nitric acid solution with the metal under consideration as cathode will give the combined effect of the specific reducing action of the cathode plus the possible catalytic action of the cathode metal. If the electrolytic reduction agrees with those obtained by the corresponding chemical reduction, the cathode metal has no catalytic action. If there is a difference between the sets of results, the difference gives us valuable information in regard to the catalytic action of the cathode metal. It will probably not be difficult then to formulate the catalytic action of the metal clearly and definitely.

The catalytic action of the metallic nitrate can be detected by adding the salt to nitric acid and then repeating the experiments with the dissolved reducing agents. These results will be supplemented by repeating the electrolytic reductions in presence of the metallic nitrate, after which there should be no difficulty in accounting for all the products obtained when the metal reacts direct with the nitric acid under the conditions of ordinary corrosion.

In some experiments, on which Mr. Milligan will report in detail later, it was found that when acidified ferrous sulphate is added to an excess of nitric acid, the main reduction product is nitric oxide. Since acidified ferrous sulphate is a weak reducing agent, this is about what one would have predicted. With a stronger reducing agent, acidified stannous chloride, the reaction runs practically completely (over ninety percent) to hydroxylamine if the temperature is kept low. If the temperature is allowed to rise, the reduction product is practically completely nitrous oxide. This has nothing to do with the stannous chloride because the same result is obtained if we heat the hydroxylamine solution and nitric acid solution. The nitrous oxide is formed by the reaction between nitrous acid and hydroxylamine

$$HNO_2+NH_2OH=N_2O+H_2O.$$

Since there is not much nitrous acid in the solution at any one time, we may have to postulate a preliminary reduction of nitric acid by hydroxylamine,

$$2HNO_3+2NH_2OH=2HNO_2+N_2O+3H_2O.$$

Acidified titanous chloride is a still more powerful reducing agent and will reduce hydroxylamine quantitatively to ammonia. It was therefore clear that it should reduce nitric acid to ammonia; but Mr. Milligan found that the main reduction product was nitric oxide, the same compound which is the chief product obtained with ferrous sulphate. In other words, titanous chloride does not reduce nitric acid so far as does the weaker reducing agent, stannous chloride. One can see what havoc this would play with any theory which made the reducing action depend solely upon the chemical potential.

The abnormal result with titanous chloride is not due to the catalytic action of the final oxidation product, because hydroxylamine is obtained on adding stannous chloride to a nitric acid solution, which has been reduced in part by titanous chloride. The next step—which has not yet been taken—is to add titanous chloride to nitrous acid, to hyponitrous acid, and to hydroxylamine, so as to determine what side reaction is catalyzed. In this particular case, it is probably the decomposition of nitrous acid which is catalyzed, though it may be that the reduction proceeds to nitrohydroxylamine[1] which then loses water, $H_2N_2O_3 = 2NO + H_2O$.

The result with titanous chloride make it possible that the data with ferrous sulphate are due in part to catalytic action. This can be checked by finding whether ferrous sulphate does or does not reduce a hyponitrous acid solution.

It is evident from what has already been done that Armstrong was right in saying that the direct reduction products are HNO_2, $H_2N_2O_2$, NH_2OH, and NH_3, while NO_2, NO, N_2O and N_2 are formed by secondary reactions, very probably as follows:—

$$HNO_3 + HNO_2 = 2NO_2 + H_2O$$
$$3HNO_2 = 2NO + HNO_3 + H_2O$$
$$H_2N_2O_3 = 2NO + H_2O$$
$$H_2N_2O_2 = N_2O + H_2O$$
$$HNO_2 + HN_2OH = N_2O + 2H_2O$$
$$H_2N_2O_2 + 2NH_2OH = 2N_2 + 4H_2O$$
$$HNO_2 + NH_3 = N_2 + 2H_2O.$$

The reaction between nitric and nitrous acids to form nitrogen peroxide will increase relatively with increasing concentration of nitric acid. It is simply the reverse of one of the reactions in the synthesis of nitric acid by the arc process. It is sometimes stated that the formation of nitrogen peroxide is due to the oxidation of nitric oxide by concentrated nitric acid; but this is clearly a mistaken way of looking at things. There is no reason to postulate an intermediate formation of nitric oxide.

We get nitric oxide by the decomposition of nitrous acid and this reaction will predominate as the concentration of nitric acid decreases and that of nitrous acid increases. This equilibrium was studied carefully by Noyes and Edgar[2] over a dozen years ago.

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[1] Angeli: Gazz. chim. ital. 26 II, 17 (1896).

[2] J. Am. Chem. Soc. 33, 292 (1911).

We get nitrous oxide either through the dehydration of hyponitrous acid or through the interaction of nitrous acid and hydroxylamine.[1] If this second reaction passes through the hyponitrous acid stage as seems probable, these are merely different ways of saying the same thing.

It is usually assumed that nitrogen comes from the interaction of nitrous acid and ammonia, apparently because ammonium nitrite will decompose into nitrogen and water under certain conditions. This seems to me inadequate because we get nitrogen evolved in cases where there is no reason to suppose that ammonia is formed at all. We must therefore postulate a reaction between hyponitrous acid and hydroxylamine.

$$H_2N_2O_2 + 2\ NH_2OH = 2N_2 + 4\ H_2O.$$

Oesterheld[2] was forced to the same conclusion when he found that the electrolytic oxidation of an alkaline hydroxylamine solution at a platinum anode gave a mixture of gases approximating 51% N_2 and 49% N_2O. "The formation of nitrous oxide is undoubtedly due to the oxidation of hydroxylamine to hyponitrous acid which then breaks down into nitrous oxide and water:

$$NH_2OH + O = NOH + H_2O$$
$$2NOH \longrightarrow H_2N_2O_2 \longrightarrow N_2O + H_2O.$$

It is impossible, however, that the nitrogen formed from the hydroxylamine can be a decomposition product of ammonium nitrite as was assumed to be the case when studying the oxidation of ammonia. In the first place there is no ammonia present and, in the second place, there can be no oxidation of hydroxylamine to nitrous acid at the low anode potential which was maintained. The simplest explanation is that the nitrogen is due to the reaction between hydroxylamine and nitroxyl which is the first oxidation product,

$$O{:}NH + NH_2OH = N_2 + 2H_2O.$$

A. Angeli has observed the same reaction when nitroxyl splits off from benzene sulphohydroxamic acid in presence of hydroxylamine. While two molecules of nitroxyl may combine to form hyponitrous acid or nitrous oxide and water, yet there is a quantitative evolution of nitrogen so long as there is a sufficient excess of hydroxylamine."

It is also possible that nitrogen may be formed simultaneously with nitrous oxide by a different decomposition of hyponitrous acid,[3] perhaps

$$5H_2N_2O_2 = 4H_2O + HNO_3 + 4N_2.$$

While it is perfectly certain that nitrogen peroxide, nitric oxide, nitrous oxide, and nitrogen are due to secondary reactions and are not direct reduction products of nitric acid, this does not mean that hydroxylamine and ammonia may not be formed by reduction of the oxides of nitrogen. In fact, we know that under certain conditions this may happen. The simplest supposition to make would be that the stages were $NO_2 \longrightarrow NO \longrightarrow N_2O(\longrightarrow N_2) \longrightarrow NH_2OH \longrightarrow NH_3$; but there seems to be good reason to believe that matters are not

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[1] V. Meyer: Ann. **175**, 141 (1875).

[2] Z. anorg. Chem. **86**, 129 (1914).

[3] Berthelot and Ogier: Compt. rend. **96**, 30 84 (1883); Hantzsch and Kaufmann: Ann. **232**, 317 (1896); Ray and Ganguli: J. Chem. Soc. **91**, 1866 (1907).

so simple as this. It seems probable that hydroxylamine is not always a preliminary stage to the formation of ammonia, that nitrous oxide is not always a preliminary stage in the formation of hydroxylamine or ammonia from nitrogen peroxide or nitric oxide, and that the reduction of nitrogen peroxide does not necessarily give rise to nitric oxide as an intermediate stage.

Divers and Shimidzu[1] have found that "zinc dissolves in dilute nitric acid, forming nitric oxide, nitrous oxide, ammonia and zinc nitrates, and sometimes a trace of hydroxyammonium [hydroxylamine] nitrate. Should it dissolve so far as to neutralise or nearly neutralise the acid, zinc nitrite is also formed. By mixing much sulphuric acid with the nitric acid, the dissolution of the zinc produces sulphates instead of nitrates and nitrites, hydroxyammonium and ammonium sulphates, nitrous oxide and a little nitrogen, little if any nitric oxide, and, lastly, hydrogen."

In this paper I shall not take up the question why sulphuric acid increases the yield of hydroxylamine, but rather why it does not appear when nitric acid alone is used. Since Divers did not check his temperatures, it is possible that the temperature rose in the experiments in which there was no sulphuric acid and that the hydroxylamine was destroyed by reaction with nitrous or nitric acid. This is not very probable and would lead to the principal product being nitrous oxide and not ammonia. Also, in presence of sulphuric acid the yield of hydroxylamine increases with rising temperature.[2]

When once formed, hydroxylamine is not reduced readily to ammonia (p. 613). "In one experiment, 10 cc of a solution of hydroxyammonium chloride containing 0.033 gram of hydroxyamine, were made up to 100 cc with water, containing a little sulphuric acid. The mixture was poured upon 45 grams of granulated zinc, and thus exposed to a relatively very large surface of zinc. It was left in contact with the zinc for two hours, dilute sulphuric acid being occasionally added, so as to keep up effervescence. The solution, still effervescing, was poured off, and titrated for hydroxyamine, and the whole of this was found unchanged. Indeed, the anomaly was observed, of a little more iodine being required than equalled the whole hydroxyamine. But we find that in presence of a concentrated solution of zinc salt, a clear excess of iodine solution is decolorised over that calculated for the hydroxyamine.

"We then tried the action of zinc alone upon a dilute solution of hydroxyammonium chloride. Here there was a marked destruction of the hydroxyamine in two hours, one-eighth to one-fourth disappearing. The nitrate appears to be somewhat more unstable. Acidified with a little sulphuric acid, however, the nitrate gave in ten minutes on zinc, a third more hydroxyamine than it contained in consequence of the conversion of part of its nitric acid to that base. (The nitrate consists by weight of one part base to two parts acid, so that about a third of its acid became hydroxyamine.) The presence of zinc sulphate or ammonium chloride or of free ammonia, appears to be without marked effect.

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[1] J. Chem. Soc. 47, 597 (1885).

[2] Divers and Shimidzu: J. Chem. Soc. 47, 619 (1885).

"Hydroxyamine is thus seen to be only very slowly decomposed by the contact of zinc with its cold solution, even in absence of acid. It was otherwise, however, in the case of hot solutions, for in these the hydroxyamine is destroyed by zinc with relative rapidity, although still wonderfully resistant to decomposition. Boiled for a quarter of an hour in 100 cc, and less, of solution, upon 35 grams of zinc, 0.033 gram was reduced to 0.02 gram. Heated to 70°-80° for one hour upon 35 grams of zinc, 0.033 gram hydroxyamine in 100 cc was reduced to 0.008 gram."

Divers and Shimidzu[1] state specifically that ammonia and hydroxylamine appear to be not consecutive products but products of parallel and independent reductions. "As pointed out in the previous paper ammonia is abundant from the first, during the reduction of nitric acid by sulphuric acid and zinc. Its non-production from hydroxyamine, in the presence, that is, of free acid, gives its appearance during this reduction a new interest. Nitrous oxide is also produced. We have made no attempt to estimate the very small quantities of this gas formed in our experiments. Deville's determinations may be referred to on this point, but we ourselves in Japan have no means of doing so, for purposes of illustration.

"A few determinations only of ammonia have been made by us, and further work in this direction is desirable. Having poured off the acid solution from the zinc at those times when it was calculated that the hydroxyamine would have just reached its maximum, one part was titrated for hydroxyamine, and another titrated for ammonia, by adding first sodium carbonate until some zinc carbonate was precipitated, then iodine to destroy hydroxyamine, then precipitating nearly all the zinc by sodium sulphide, and distilling the mother-liquor with potassium hydroxide. The ammonia was received in acid and titrated. In this way we obtained ammonia equivalent to much of the nitric acid not convertible into hydroxyamine.

"By using a very great excess of sulphuric acid nearly, if not all, the nitric acid unconverted to hydroxyamine appears to be converted into ammonia. This is in accordance with Kinnear's results,[2] and we believe it to be correct, but there is difficulty in determining closely a very small quantity of ammonia in presence of very much zinc salt, and, without more trials than we have made, we cannot assert that it is so.

"Under favourable conditions, we have got as much as, and even more than seven-tenths of the nitric acid converted to hydroxyamine, but, with unsuitable zinc, we have sometimes failed to get more than two-tenths converted. In our former paper, we mentioned a yield of eight-tenths of the nitric acid as hydroxyamine, but we were not confident as to this yield having been really obtained.

"In a preceding section, we have attributed the production of hydroxyamine entirely to the specific action of the zinc and the nitric acid upon sulphuric acid. We can now almost assert that ammonia is not a product of that

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[1] J. Chem. Soc. **47**, 615 (1885).

[2] Kinnear: Chem. News, **46**, 63 (1882).

specific action, and that the ammonia freely produced from the first during the dissolution of the zinc in the mixed acids, is formed solely by the direct action of the nitric acid upon the zinc. Uncertainty thus seems cleared away as to the specific hydrogenising action of the sulphuric acid upon the nitric acid. For, although nitric acid in contact with zinc and water can readily hydrogenise itself without the aid of any other acid, the product is then ammonia, not hydroxyamine, whereas when nitric acid is hydrogenised by sulphuric acid, the product is hydroxyamine and not ammonia.

"In the paper on the production of hydroxyamine from nitric acid, we have said that a perfect metal for making hydroxyamine would be one active towards dilute nitric acid, inactive towards sulphuric or hydrochloric acid, and inactive towards hydroxyamine. With our present knowledge we would alter this, and say, that such a metal should be inactive to nitric acid alone, and active only to a mixture of nitric acid with either hydrochloric or sulphuric acid. The above considerations at once explain why it is that a metal may freely produce ammonia from nitric acid and yet produce hydroxyamine from it only with difficulty, or not at all. For, in such cases, there may be strong action of the metal upon nitric acid, or independently upon both acids, whereby ammonia will be formed; and yet be no specific action upon the two acids combined, which would give rise to hydroxyamine. Or again, the effect of this specific action may be as nothing compared with that of the superior activity of the metal towards the independent acids.

"Granulated zinc may differ widely in its power of yielding hydroxyamine, but a given preparation of it, or mixtures of similar preparations, will show under the same circumstances the same power at one time that it has shown at another. The differences observed in this relation between different preparations of granulated zinc, depend in part upon the nature of the zinc melted down, of course, but they also depend upon differences in the process of granulating. Partly, no doubt, in consequence of the fact that apparently both the condition of the zinc before it has been granulated, and the character of the operation of granulating it, may exert marked influence upon its power to produce hydroxyamine from nitric acid, but at any rate we have failed in the attempts we have made to secure at will granulated zinc of a uniform and high power in this respect, or to ascertain any sufficient knowledge of the causes of its varying power.

"On one occasion, there seemed to us to be a marked difference between the same zinc when granulated at diffreent temperatures. By running the zinc when almost boiling hot, and then again, from the same melting, after the zinc had cooled almost to the solidifying point, a much more productive lot of granules was obtained from the second running than from the first. But on trying the effect of this difference in operating again and again, we got no confirmation of our first result. We also varied the process by pouring from a height, and pouring near the water, and of granulating in boiling water and granulating in cold water, but from all our trials we learnt nothing. At one spell of work we could repeatedly granulate zinc turning out to be of nearly equal power, but on another occasion we could not count on producing more zinc of the same power."

There is independent confirmation of the view that the formation of ammonia does not always pass through the hydroxylamine stage. Tafel[1] says that "nitric acid in sulphuric solution is reduced electrolytically at an amalgamated cathode almost exclusively to hydroxylamine, although such a cathode has a distinct electrolytic reducing action on hydroxylamine sulphate. On the other hand nitric acid is reduced almost completely to ammonia at a copper cathode which is effective only at low current densities and which is quite inadequate to reduce hydroxylamine sulphate any further.

"From these facts the only safe conclusion to draw is that the electrolytic reduction of nitric acid to ammonia at a copper cathode does not pass through the hydroxylamine stage. . . . I assume that certain cathode materials, such as copper for instance, by a chemical action divert the reduction process somewhere between nitric acid and hydroxylamine from the specific electrolytic course, so that the reaction goes direct to ammonia, passing round the hydroxylamine stage. I cannot tell certainly at what stage this switch takes place; but it seems not improbable that it occurs at dihydroxylamine, $NH(OH)_2$."

There is another way in which one can get ammonia without passing through the hydroxylamine stage. Hantzsch and Kaufmann[2] found that hyponitrous acid may break down either to give nitrous oxide or to give ammonia,

$$H_2N_2O_2 \longrightarrow N_2O+H_2O$$
$$3H_2N_2O_2 \longrightarrow 2NH_3+N_2O_3.$$

Any substance, which catalyzed the second reaction without catalyzing either the first one or the reduction to hydroxylamine, would give ammonia. We do not know yet what actually happens; but it seems certain that hydroxylamine is not necessarily an intermediate stage in the formation of ammonia. Hantzsch[3] suggests that the syn form of hyponitrous acid would be expected to split off water very easily; but he leaves it rather vague as to what the characteristics of the anti form would be.

We find other difficulties with nitric oxide and nitrogen peroxide. Divers and Haga[4] say that "every chemist is supposed to know that when nitric oxide is passed into a hydrochloric acid solution engaged in dissolving tin, ammonia and hydroxylamine are produced. Strictly speaking, however, this is by no means the case. We assert that, in the change that goes on, not a trace of ammonia is formed. Experience to the contrary must have been all vitiated by neglecting to exclude air while the gas was in contact with the mixture, and to use pure nitric oxide. Hydroxylamine is formed, but if the nitric oxide never comes in contact with oxygen, not a trace, as we have said,

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[1] Z. anorg. Chem. 31, 289 (1902).
[2] Ann. 293, 332 (1896).
[3] Ann. 292, 340 (1896).
[4] J. Chem. Soc. 47, 623 (1885).

of ammonia is formed. V. Dumreicher has already shown that acid stannous chloride will of itself convert nitric oxide to hydroxyamine; whether he then found ammonia or not we cannot learn. This will have depended upon the care with which he excluded air. But his observation was of great interest at the time, as serving to show what little foundation there was for the hypothesis of the action of nascent hydrogen in explaining the formation of hydroxyamine from nitric oxide by treating it with tin and hydrochloric acid. So far, indeed, as we can ascertain by experiments which we have made, the presence of the metal does not directly help to form hydroxyamine, and is of no service but to generate stannous chloride. It is objectionable on two grounds; it leaves the solution charged with unused stannous chloride whenever the preparation of hydroxyamine is stopped; and, secondly, the hydrogen it produces carries off the nitric oxide that would otherwise lie on the surface of the solution and be absorbed.

"Tin and hot concentrated hydrochloric acid do not sensibly destroy hydroxyammonium chloride. This is our experience, and it confirms that of Mr. Shimidzu and one of us, as to the want of action of zinc and sulphuric action upon the hydroxyamine. Further stannous chloride in acid solution has no action upon the hydroxyammonium chloride, even when boiled with it; that is, for a reasonable time; an aqueous solution could itself not be boiled very long without suffering some change. Were either tin and hydrochloric acid, or stannous chloride, capable of converting hydroxyamine into ammonia, what we assert concerning the non-production of ammonia from nitric oxide by tin and hydrochloric acid could not, of course, be true. According to V. Dumreicher, however, at a temperature of 100°, hydroxyamine is quickly and completely reduced to ammonia by excess of stannous chloride.

"Coming now to the use of stannous chloride, our experience is, that with exclusion of air, not a trace of ammonia is formed by its action upon an acid solution of hydroxyamine. In working, we prefer to use a mixture of ferrous sulphate, nitric acid, and sulphuric acid as the source of the nitric oxide. It yields the gas in a pure state, and the generator can be charged and worked so as to furnish easily, except for a short time at first, a gentle stream of the gas for 24 hours at a stretch. To destroy any nitric peroxide, formed through entrance of traces of air into the generator, the gas is sent through a wash-bottle of potassium hydroxide solution. This bottle is scarcely necessary, however, as reaction between ferrous sulphate and the acids does not begin in the cold; and before starting the disengagement of nitric oxide, a current of hydrogen is sent through the whole series of flasks and bottles until all air has been driven out. Only then is the evolution of nitric oxide commenced and passed into the apparatus, the current of hydrogen being at the same time discontinued. The remote end of the arrangement is provided with a wash-bottle as a guard against any reflux of air. When the process is finished, or when it has to be interrupted, the current of nitric oxide is stopped and its place taken by one of hydrogen again, until all nitric oxide has been chased away. The flasks of tin chloride may then be opened with impunity, air having no effect upon the hydroxyamine already formed, not even when stannous chloride is still present, and being so, goes on changing into the stannic salt by contact with the air.

"The reaction between acid stannous chloride and nitric oxide is not quite simple, however. The greater part of the nitric oxide becomes hydroxyammonium chloride, but a part of it is always converted into nitrogen. No nitrous oxide is formed. Since much of the nitric oxide passes unabsorbed, we could not well take the proportions of it to the hydroxyamine formed at the same time. But we many times collected it in quantity, the nitric oxide we were using being tested and found pure, as from its source it was sure to be. . . .

"There is a remarkable fact about the reaction between nitric oxide and stannous chloride, we have yet to mention. At a temperature of fully 100°, there is no action between nitric oxide and acid stannous chloride solution. The stannous chloride remains unchanged[1] for hours together, and neither nitrogen nor hydroxyamine is formed. The only thing we have noticed is always a trace of ammonia in experiments at 100°, and this, we are inclined to believe, is due to some other cause than this reaction alone. At 90°, the action is still exceedingly small, but as the temperature descends from about 80°, it becomes rapidly greater with the descent.

"We have tried cooling the tin-solution by a freezing mixture, but have not succeeded in getting better results than at the ordinary temperature. Further experiments are needed, to be sure that a low temperature does not favour the reaction. . . .

"When nitric acid is in presence of enough water to prevent any reaction taking place between it and hydrochloric acid, it is not perceptibly acted upon by stannous chloride. It may be left for a day or two mixed with these reagents, and remain, as well as the stannous chloride, unchanged. We have not yet established this fact by quantitative estimation, air having been allowed access to the mixture in our experiments hitherto, but we have no reason to believe that it is incorrect.

"If such a mixture is sufficiently dilute, it may even be boiled without change, but if not too dilute, reaction is thus set up. Another way of bringing about reaction in such a dilute solution, is to add sulphuric acid, already slightly diluted so that the heating effect of mixing it with water may be avoided, since that alone would afford an explanation of its action. It is thus seen that the addition of sulphuric acid, by diminishing the weakness of the solution in acid, serves to induce the reaction between the tin salt and the nitric and hydrochloric acids.

"When dilute nitric acid added to the solution of stannous chloride in hydrochloric acid is not too dilute, reaction between them proceeds and continues until either the stannous chloride has all become stannic chloride, or

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[1] [Mr. Milligan suggests that this may be due chiefly to the sparing solubility of nitric oxide at the higher temperature.]

until the solution has become too dilute in hydrochloric acid. In the latter case, we believe that we can cause the reaction to go on again, by passing hydrochloric acid gas into the solution, but we have not tried that yet. We have only at present added sulphuric acid as mentioned above with very favourable results. We have not succeeded, however, in destroying all nitric acid.

"The reaction which takes place results in the conversion of so much of the nitric acid as is decomposed into hydroxyammonium chloride and nothing else—no ammonia and no gaseous body, provided the stannous chloride remains in excess. This statement is in direct opposition to that made by von Dumreicher, which is, that "acid stannous chloride acting on nitric acid yields hydroxylamine, but the reaction proceeds further, and the hydroxylamine is nearly simultaneously reduced to ammonia." When the stannous chloride is in insufficient quantity, the conversion of the last portion of it is followed, first, by the solution becoming yellow and smelling of nitrosyl chloride, and then by an effervescence of nitrous oxide. If, on the disappearance of this yellow colour, more stannous chloride is at once added, the solution is at once bleached; and if this additional quantity of stannous chloride is insufficient, the liquid again becomes yellow after a time. The phenomena observed in this case, in fact, strongly remind one of those noticed by Vernon Harcourt[1], in a solution of hydrogen peroxide and hydrogen iodide to which sodium thiosulphate is added each time coloration by iodine reappears. When we proceeded in this way, the solution soon became charged with nitrous oxide, which escaped with effervescence on stirring."

If Divers is correct in saying that nitric oxide is not reduced to ammonia by acidified stannous chloride and that ammonia is formed to some extent in presence of nitrogen peroxide, this means that the reduction of nitrogen peroxide by acidified stannous chloride does not pass through the nitric oxide stage. As there are no data to show whether the amount of ammonia is or is not equivalent to the amount of nitrogen peroxide, we do not know whether the ammonia is formed from N_2O_3 or from the hypothetical first reduction product of nitrogen peroxide, NO_2H_2. This reaction should be studied experimentally as soon as possible. Mr. Milligan does not feel certain that Divers is right and von Dumreicher wrong in the points at issue between them.

If nitrous oxide is formed solely as a dehydration product of hyponitrous acid, we ought to get it on reduction of nitric oxide and under favourable conditions. If it is formed from the reaction between hyponitrous acid and hydroxylamine this would not be the case, because there is no hyponitrous acid when we start with nitric oxide. As a matter of fact we do not know at all what is the first reduction product of nitric oxide. The most probable product is hyponitrous acid; but in that case there is no apparent reason why Divers should not have obtained some nitrous oxide. The whole matter of the reduction of nitric oxide calls for systematic study.

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[1] J. Chem. Soc. 20, 460 (1861).

Guye and Schneider[1] have shown that at 280° nitrous oxide is reduced very slowly relatively to nitric oxide by nickel and hydrogen and that no nitrous oxide is formed during the reduction of nitric oxide. Nitrous oxide is evidently not ordinarily an intermediate stage in the formation of hydroxylamine, ammonia, or nitrogen from nitric oxide. The reduction to nitrous oxide can be carried out by means of sulphurous acid.[2]

"Two molecules of nitric oxide react with one of sulphurous acid over water in several hours to form aqueous sulphuric acid and one volume of nitrous oxide; but, according to R. Weber, the change is not complete even after fourteen days and it is not rapid at the temperature of the lead chamber. In presence of platinum black, the reduction to nitrous oxide and even to nitrogen takes place readily, the rate of reaction increasing with rising temperature. According to Lunge the dry gases do not react; but, in presence of water, there is a powerful reaction which causes a complete conversion to nitrous oxide when there is an excess of sulphurous acid present, no nitrogen being formed. . . . A mixture of nitric oxide, sulphurous acid and oxygen always gives some nitrous oxide in presence of water even though there be a large excess of oxygen; in presence of sulphuric acid of specific gravity 1.32, there is no appreciable trace either of nitrous oxide or of nitrogen.

"When nitric oxide is mixed with an equal volume of hydrogen sulphide, there is a decomposition in the course of a few hours into ammonium sulphide with a small amount of nitrous oxide." It seems probable that nitrous oxide is not in this case an intermediate product in the ammonia formation.

The method of formation of nitrogen from nitric oxide is not settled definitely for all cases. Felgate[3] shows that nitric oxide and colloidal nickel react to form nitrogen and nickel oxide. In this case there is no proof of any intermediate hydrogenation, though this may occur. Since acidified stannous chloride reduces nitric oxide to hydroxylamine, we must postulate hydrogenation. If we are going to have hydrogen add on two by two with the splitting off of water, as seems to occur with nitric acid, we are rather forced to postulate some such reactions as the following:

$$2NO+2H_2 \longrightarrow (HNOH)_2 \longrightarrow N_2+2H_2O$$

$$(HNOH)_2+H_2 \longrightarrow 2NH_2OH$$

$$(HNOH)_2+2H_2 \longrightarrow N_2H_2+2H_2O$$

$$(HNOH)_2+3H_2 \longrightarrow 2NH_3+2H_2O.$$

Since ammonia is probably not formed through reduction of hydrazine, it would simplify matters if we could write the last reaction:

$$2NO+5H_2 \longrightarrow 2HNOH+3H_2 \longrightarrow 2NH_3+2H_2O.$$

The difficulty with this is that it is purely paper work and that we have no proof of any of these stages. I hope that this formulation of the problem may prove to be the first step in the solution. Sabatier and Senderens[4] report that palladium sponge and hydrogen reduce nitric oxide completely to ammonia.

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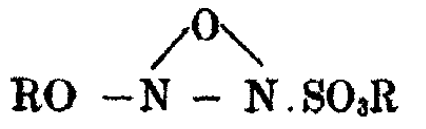
[1] Helvetica chim. Acta, 1, 133 (1918).

[2] Spiegel: "Der Stickstoff," 89 (1903).

[3] Chem. News. 108, 178 (1913).

[4] Compt. rend., 114, 1429 (1892).

The last paragraph has brought up the question of hydrazine which is usually not assigned any definite place among the reduction products of nitric acid. Hantzsch[1] considers that the salts of dinitrososulphonic acid have the formula



$$\mathrm{RO}-\overset{\diagup\,\mathrm{O}\,\diagdown}{\mathrm{N}\;-\;\mathrm{N}}.\mathrm{SO_3R}$$

and Duden[2] showed that potassium dinitrososulphonate gives hydrazine when reduced at 0° with sodium amalgam or with zinc dust and ammonia.

$$\mathrm{KO.N_2O.SO_3K+4H_2 \longrightarrow N_2H_4+K_2SO_3+2H_2O.}$$

According to Spiegel,[3] careful reduction with sodium converts hydrazine into ammonia.

It was found by von Brackel[4] that hydrazine is obtained when a solution of sodium bisulphite, silver hyponitrite, and hydrochloric acid (the acid being equivalent to the silver) is reduced with zinc dust and glacial acetic acid in the cold. The hydrazine was not isolated as such, but a yellow precipitate of benzalazine was obtained on adding benzaldehyde. The presence of sulphite is apparently essential, just as the presence of sulphuric acid is desirable in the reduction of nitric acid to hydroxylamine. I should like to see the experiment tried of running nitric acid with and without nitrous acid slowly into a cold, concentrated solution of sulphurous acid.

According to Spiegel,[5] "sulphurous acid reduces nitric acid very slowly unless sulphuric acid is present. If one boils one volume of nitric acid (sp.gr. 1.4) with five volumes of aqueous sulphurous acid, nitric and nitrous oxides are formed; in presence of less water there is a sudden, violent evolution of nitric oxide before boiling begins. A mixture of nitric and sulphuric acids reacts with sulphurous acid in different ways, depending on the concentration. If sulphur dioxide is passed into a mixture of oil of vitriol with ten percent of strong nitric acid, lead chamber crystals are formed if the saturated mixture is left to itself for twenty-four hours. If these are redissolved and more sulphur dioxide is passed in, the liquid becomes dark violet if left standing in a tightly closed bottle, and contains a mixture of sulphurous acid, which passes off in the air or in a vacuum, and nitrous acid.[6] A mixture of nitric acid and dilute sulphuric acid (at least sp.g. 1.34) is readily reduced by sulphurous acid to nitric oxide. If one drops liquid sulphurous acid into pure nitric acid monohydrate, there are formed red fumes and lead chamber crystals, which disappear again when an excess of the reducing agent is added, so that finally there is only a slightly colored sulphuric acid. On heating a mixture of the two acids, Frémy observed a formation of nitrous oxide. . . .

"Hydrogen sulphide is not attacked at ordinary temperature by nitric acid containing no oxides of nitrogen, and there is no reaction when hydrogen

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[1] Ber. 27, 3264 (1894).

[2] Ber. 27, 3498 (1894).

[3] "Der Stickstoff," 571 (1903).

[4] Ber. 33, 2115 (1900).

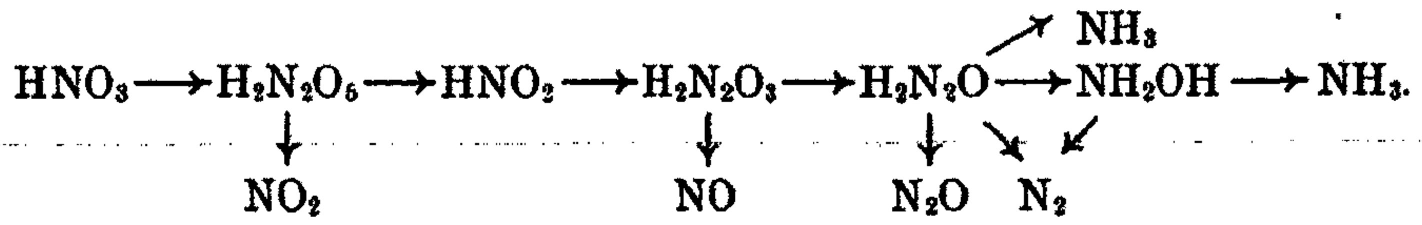
[5] "Der Stickstoff," 223, 102 (1903).

[6] Girard and Pabst: Bull. (2) 30, 531 (1878).

sulphide is passed into a pure acid of 1.18 sp. g. If the nitric acid contains only so much of the oxides of nitrogen as forms on standing exposed to air at 25°, the whole of the acid will be decomposed with formation of sulphur, sulphuric acid, ammonia, nitric oxide, and nitrogen."

"Nitrous acid in a good deal of water loses two thirds of its oxygen in presence of sulphurous acid and is reduced to nitrous oxide. When less water is present or when sulphur dioxide is passed into a solution of nitric acid in sulphuric acid of 1.4 sp.g., nitric oxide is formed. Nitrous acid dissolved in oil of vitriol does not react at all with sulphurous acid."

Mr. Milligan believes that there is some reason for postulating the intermediate existence of the hypothetical acid, $H_2N_2O_5$. He suggests writing the main chain of reductions:



$$\begin{tikzcd}
 & & & & & NH_3 & \\
HNO_3 \arrow[r] & H_2N_2O_5 \arrow[r] \arrow[d] & HNO_2 \arrow[r] & H_2N_2O_3 \arrow[r] \arrow[d] & H_2N_2O \arrow[r] \arrow[d] \arrow[ru] \arrow[rd] & NH_2OH \arrow[r] \arrow[d] & NH_3. \\
 & NO_2 & & NO & N_2O & N_2 &
\end{tikzcd}$$

When this work was reported at the intersectional meeting of the American Chemical Society held in Syracuse in February, Professor R. A. Baker suggested that another factor to be taken into account was the direct oxidizing action of nitric acid at any rate in concentrated solutions. This is the point of view taken by Freer and Higley[1] and we know that nitrogen peroxide will oxidize iron[2] to passive iron. While not denying the possibility of direct oxidation, which one must assume if one puts carbon in fused potassium nitrate, I see no reason at present for postulating anything but electrolytic corrosion under all ordinary conditions. It will be soon enough to modify this hypothesis when it has proved inadequate. Postulating a second hypothesis unnecessarily gives rise to indecision and delay.

The general results of this paper are:—

1. The action of nitric acid on metals can be considered profitably as a case of electrolytic corrosion, the anode reaction being the formation of the nitrate. This is the view advocated by Armstrong in 1877.

2. The nature of the metal shows itself in at least three ways: in the reducing power as measured by over-voltage; in the catalytic action of the metal; and in the catalytic action of the salt of the metal. These three factors are to be studied in detail.

3. Acidified ferrous sulphate reduces nitric acid practically completely to nitric oxide; acidified stannous chloride reduces it practically completely to hydroxylamine; acidified titanous chloride, though a stronger reducing agent than stannous chloride, reduces nitric acid mainly to nitric oxide.

4. The direct reduction products of nitric acid are nitrous acid, hyponitrous acid, hydroxylamine, and ammonia, while nitrogen peroxide, nitric

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[1] Am Chem. J. **15**, 71 (1893); **17**, 18 (1895); **18**, 587 (1896); **21**, 377 (1899).

[2] Young and Hogg: J. Phys. Chem. **19**, 617 (1915).

oxide, nitrous oxide, and nitrogen are due to secondary reactions. This is the view advocated by Armstrong in 1877.

5. Hydroxylamine is not necessarily an intermediate stage in the formation of ammonia and nitric oxide is apparently not a necessary stage in the reduction of nitrogen peroxide, though the evidence in regard to the latter point needs confirmation.

6. In the ordinary reduction of nitric acid, nitrogen probably occurs as the result of a reaction between hydroxylamine and hyponitrous acid more often than as the result of a reaction between nitrous acid and ammonia. In the reduction of nitric oxide, it seems possible that nitrogen may result from the dehydration of a hypothetical substance, NHOH or $(NHOH)_2$.

7. Nitrous oxide is not ordinarily a direct reduction product of nitric oxide and it is probably never an intermediate stage in the reduction of nitric oxide to hydroxylamine, ammonia, or nitrogen.

8. Hydrazine is a direct reduction product of hyponitrous acid; but is not ordinarily an intermediate stage in the formation of ammonia. The presence of sulphite is apparently essential to the formation of hydrazine.

9. The presence of sulphuric acid increases the tendency to form hydroxylamine during the reduction of nitric acid; but no satisfactory explanation of this has yet been offered.

10. While it is probable that nitrous oxide results, ordinarily from the dehydration of the syn form of hyponitrous acid, it is not known what the relation is between the syn and anti forms on the one hand and the production of hydroxylamine, ammonia, nitrogen, and hydrazine on the other hand.

Cornell University.

THE SOLUBILITY OF GASOLINE (HEXANE AND HEPTANE) IN WATER AT 25°C[1]

BY LOWELL H. MILLIGAN[2]

In connection with an investigation of a method for analyzing air for gasoline vapor, it was necessary to determine the solubility of gasoline vapor in water at 25°C. From the data obtained and the vapor pressures of hexane and heptane at 25°C., it has been possible to calculate the approximate solubility of liquid hexane and heptane in water at this temperature. The results differ so greatly from the meager data available in the literature, that they are presented here.

Herz[3] determined the miscibility of ligroin with water and of benzene with water, and found that at 22°C.:

100 vol. of water dissolve 0.341 vol. liquid ligroin.
100 vol. of water dissolve 0.082 vol. liquid benzene.

If it be assumed that ligroin is a light petroleum distillate, its solubility should be of the same order of magnitude as that of casing-head gasoline.

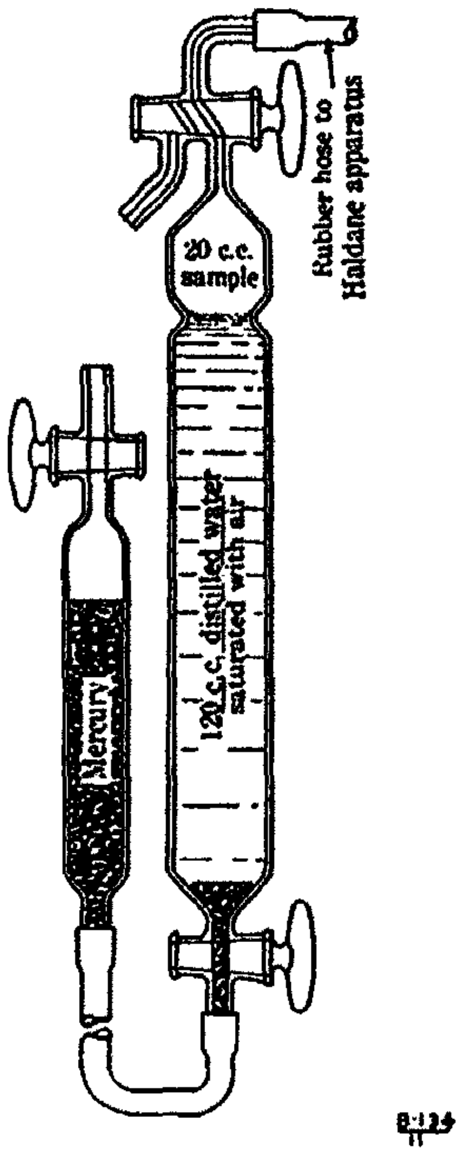

Fig. 1
Glass Apparatus for the Determination of the Solubility of Gasoline Vapor in Water at 25°C.

In the present work the solubility of gasoline vapor in water was first determined. This was done by preparing a stable mixture of the vapor and air by completely evaporating with electric heat a little of the gasoline in a gas-tight box and thoroughly mixing the gases with an electric fan. A sample of this mixture was analyzed accurately several times by combustion in a Bureau of Mines type of Haldane gas analysis apparatus. The average of these analyses was assumed to represent the true composition of the sample. Twenty cubic centimeters of the sample were introduced into the glass apparatus shown in Fig. 1, which was kept at 25°C. by immersion in a water bath agitated with air and maintained at this temperature, and the stopcocks were closed after the sample was adjusted to approximately atmospheric pressure. The apparatus was then removed from the water bath and shaken violently up and down for two minutes, which was a sufficient time to bring about

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[1] Published by permission of the Director, Bureau of Mines, Department of the Interior.

[2] Consulting Chemist, Pittsburgh Experiment Station, Bureau of Mines.

[3] Herz: Ber. 31, 2669 (1898).

Table I

Calculations for the Solubility of Hydrogen, Pittsburgh Natural Gas, Motor Gasoline Vapor, Casing-head Gasoline Vapor and Benzene Vapor, in Water at 25° C.

(a) Gas	(b) Average formula of vapor sample	(c) No.	(d) % in original sample	(e) % after shaking with water	(f) Gas originally present in 20 c.c. sample 20(d). (c.c.)	(g) Gas present after shaking with water 20 (e) (c.c.)	(h) Gas dissolved (f)-(g) (c.c.)	(i) $S_{25^\circ} = \frac{20(h)}{120(g)}$	(j) Solubility coefficient, $\alpha_{25^\circ C.}$ Calc. $\left((i)\times\frac{273}{298}\right)$	From tables
Hydrogen	H_2	1	3.885	3.495						
		2	3.862	3.485						
		Av.	3.875	3.490	0.775	0.698	0.077	0.0184	0.017	0.0175
Pittsburgh Natural Gas	90% CH_4	1	3.49*	2.87*						
	10% C_2H_6	2	3.47	2.94						
		3	—	2.84						
		4	—	2.81						
		Av.	3.48	2.87	0.696	0.574	0.122	0.0354	0.032	0.0311**
Motor Gasoline (66° Be)	C_7H_{16}	1	0.457	0.417						
		2	.477	.420						
		3	.463	—						
		Av.	.466	.419	0.0932	0.0838	0.0094	0.0187	0.017	—
Casing-head Gasoline (81° Be)	C_6H_{14}	1	.897	.833						
		2	.877	.803						
		Av.	.887	.818	0.177	0.164	0.013	0.0132	0.012	—
Benzene.	C_6H_6	1	1.63	0.15	0.326	0.030	0.296	1.64	1.5	—

*Values for total hydrocarbons present.
**Calculated from values for CH_4 and C_2H_6.

equilibrium, and the residual gas was transferred to the Haldane apparatus and analyzed. From the average result of several such procedures the absorption coefficient of the gasoline vapor in water at 25°C. was calculated.

The results obtained by this method for motor gasoline, casing-head gasoline, and also for hydrogen, Pittsburgh natural gas (90% methane and 10% ethane) and benzene, are given in Table I. Hydrogen and Pittsburgh natural gas were used in order to check the method against known data. The gasoline samples were straight petroleum distillates; the motor gasoline distilled between 45° and 206°C., with an average boiling point of 119°C. at 747 mm. pressure; the casing-head gasoline distilled between 33° and 126° C. with an average boiling point of 62°C. at 743 mm. pressure. The average hydrocarbon present in the motor gasoline vapor sample was slightly over C_7H_{16} and that in the casing-head gasoline vapor sample was slightly under C_6H_{14}. In making the calculations of solubility the total pressure has not been corrected to exactly 760 mm. of mercury, nor has the small volume change in the sample due to the changes in the partial pressures of the oxygen, nitrogen, and the combustible gas been taken into account, because these factors are within the experimental error of the method, and would not appreciably affect the final results which are expressed to only two significant figures.

The agreement between the values of the solubility coefficient determined in this way for hydrogen and Pittsburgh natural gas, and the values obtained from tables of solubility, shows that the method gives satisfactory results. The solubility coefficient $\alpha_{25°C.}$ represents the volume of the gas or vapor reduced to 0°C., which will dissolve in one volume of water at 25°C. when the pressure of the gas over the water is 760 mm. Although this condition cannot actually exist with gasoline or benzene, since in these cases the vapor pressure of the liquid is considerable less than 760 mm. at 25°C., nevertheless the coefficients can be compared to similar coefficients for true gases, and can be satisfactorily used in calculations involving the lower vapor pressures which are experimentally obtainable.

The solubility of gasoline vapor in water is considerably less than was expected from reasoning based on the fact that ethane is more soluble than methane. Apparently, however, as the molecular weight of the paraffine hydrocarbons increases, the corresponding solubility by volume first increases then decreases to values lower than those for methane, and then increases slightly again between hexane and heptane. The calculation of the solubility of benzene vapor was made on the basis of only one analysis and is consequently less accurate than the other determinaitons.

From the values of the solubility coefficients for gasoline vapor of composition corresponding to hexane and heptane, and for benzene vapor, it is possible to calculate the approximate value for the solubility of liquid hexane, heptane, and benzene in water at 25°C. These calculations[1] lead to the values:

100 vol. water dissolve 0.0014 vol. liquid hexane.
" " " 0.0007 " " heptane.
" " " 0.07 " " benzene.

Herz's value for the miscibility of ligroin in water is more than one hundred times larger than the solubility of hexane or heptane determined in this way, and it is probable that he was dealing with a partial emulsion of ligroin in water, which was not broken down completely under the conditions of his experiments. The value he obtains for benzene is of the right order of magnitude, and shows that there was little, if any, emulsification of the benzene.

The method given in this paper is of general use for determining the true solubility of a sparingly soluble liquid which has an appreciable vapor pressure, and should be of special value in distinguishing between true solubility and emulsification in cases to which it can be applied. The fact that the coefficients representing the solubility in water at 25°C., for methane, ethane, hexane, and heptane, change in an irregular manner, shows that this solubility is not a continuous simple function of the molecular weight of the paraffine hydrocarbons.

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[1] The volume of hexane, say, dissolved in water in equilibrium with liquid hexane, will be the amount dissolved when the partial pressure of the hexane vapor in equilibrium over the solution, is equal to the vapor pressure of liquid hexane. Therefore, if V is the volume of the hexane vapor considered as a perfect gas reduced to 0°C., dissolved per cubic centimeter of water in equilibrium with liquid hexane at 25°C.:

$$V = \frac{\alpha_{25^\circ\text{c.}} \times (\text{vap. press. liquid})_{25^\circ\text{c.}}}{760}$$

The weight of this vapor, W, in grams per 100 cc. of water, is:

$$W = \frac{100\,\alpha_{25^\circ\text{c.}}\ \text{x}(\text{vap. press. liquid})_{25^\circ\text{c.}} \times (\text{molec. wt.})}{760 \times 22{,}400}$$

The volume of liquid hexane, v, which 100 cc. of water at 25°C. will dissolve, is therefore:

$$v = \frac{100\,\alpha_{25^\circ\text{c.}} \times (\text{vap. press. liquid})_{25^\circ\text{c.}} \times (\text{molec. wt.})}{760 \times 22{,}400 \times (\text{density liquid})_{25^\circ\text{c.}}}$$

Approximate values for use in this formula are:

	(density liquid)$_{25^\circ\text{c.}}$	(vap. press. liquid)$_{25^\circ\text{c.}}$
Hexane	0.66	150 mm
Heptane	0.70	46 "
Benzene	0.87	95 "

BLUE EYES

BY CLYDE W. MASON[1]

For a long time it has seemed highly probable that blue eyes owe their color to structure rather than to a blue pigment. Brücke[2] appears to have made the first statement regarding this. "There is no blue pigment in the iris of blue-eyed persons; but it looks blue because there is a dark pigment behind the whitish, transparent tissue. Later he[3] recognized the blues of turbid media in an extensive paper; but did not apply this to the question of blue eyes. In 1866 Helmholtz[4] stated that "the stroma may contain pigment, resulting in brown; otherwise it appears blue like a turbid medium in front of a black background." Tyndall[5] and Rood[6] have concurred in this. Quite recently Bancroft[7] has assembled the statements of some other writers on this subject and has pointed out the conflict of their views with the older ones, and the necessity for an experimental study of the subject.

Roberts[8] says: "The iris, on which the color of the eye depends, is a thin membranous structure composed of unstriped muscular fibers, nerves, and blood-vessels, held together by a delicate network of fibrous tissue. On the inner surface of this membrane there is a layer of dark purple pigment called the *uvea* (from its resemblance to the color of a ripe grape), and in brown eyes there is an additional layer of yellow(and perhaps brown-red) pigment on its outer surface also, and in some instances there is a deposit of pigment among the fibrous structures. In the albino, where the pigment is entirely absent from both surfaces of the iris, the bright red blood is seen through the semi-transparent fibrous tissues of a pink color, and in blue eyes, where the outer layer of pigment is wanting, the various shades are due to the dark inner layer of pigment—the *uvea*—showing through fibrous structures of different densities or degrees of opacity. The eyes of new-born infants of both white and black races (and I believe the new-born of all the lower animals) are dark blue in consequence of the greater delicacy and transparency of the fibrous portion of the iris; and as these tissues become thickened by use, and by advancing age, the lighter shades of blue, and finally gray are produced; the gray, indeed, being chiefly due to the color of the fibrous tissues themselves. In gray eyes, moreover, we see the first appearance of the superficial layer of yellow pigment

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[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Sitz. Akad. Wiss. Wien, Abt.I, 7, 802 (1851).

[3] Brücke: Sitz. Akad. Wiss. Wien, Abt.I, 9, 530 (1852).

[4] Handbuch der physiologischen Optik, 1, 15 (1866).

[5] Phil. Mag. (4) 37, 393 (1869); "Fragments of Science: The Sky" (1888).

[6] "Modern Chromatics", 58 (1879).

[7] J. Phys. Chem. 23, 356 (1919).

[8] Brit. Ass. Reports. 50, 135 (1880).

in the form of isolated patches situated around the margin of the pupil, or in rays running across the iris. In the hazel and brown eyes the uvea and the fibrous tissues are hidden by increasing deposits of yellow and brown pigment on the anterior surface of the iris, and black eyes result when this is very dense. It is very doubtful, however, whether the iris is ever so dark colored in the inhabitants of this country as to justify the term black being applied to it, and the popular use of the expression has reference to the widely dilated pupil common in persons with dark brown eyes. The nearest approach to a black eye among us is the dark blue or violet eye associated with black hair in some Irish adults; here the color is probably not due entirely, as in infants, to the greater transparency of the fibrous structures, but to interstitial deposits of black pigment, or to a layer situated on the anterior surface of the iris."

This view-point seems to have been adopted by the biologists[1] and to be disputed by the medical men.

One physician writes that "the color of the iris is dependent upon two factors, namely, the amount of pigment in the pigment epithelium on the back of the iris and the amount and distribution of the pigment in the stroma of the iris. The pigment granules are all practically of the same color, dark brown. [The layer of dark purple pigment, called the *uvea* from its resemblance to the color of a ripe grape, is apparently a myth.] In some albinos the iris is entirely free from pigment and appears pink. In all other cases the pigment epithelium is so densely packed with pigment that, seen by itself, it appears black. A blue iris appears so because the stroma is free from pigment and the pigment epithelium is seen through the translucent stroma and appears blue just as veins appear blue when seen through a delicate skin. All other colors of the iris are dependent upon the amount of pigment in the stroma; if this is abundant, as in the negro, the iris appears black. Practically all infants are born without any pigment in the stroma so that their eyes are blue. The thickness of the iris varies in different eyes and in different places in the iris, and also varies with the dilatation of the pupil. After Zenker's fixation there is practically no shrinkage of the iris, and measurements that I have made after such fixation show the iris to measure 0.4-0.6 mm in thickness. I know of no measurements made on frozen sections of fresh eyes."

Pouchet considered the blues of turbid media exhibited by various tissues to be related to fluorescence and named the phenomenon *cérulescence*. Mandoul[2] takes issue with him and has established the nature of Tyndall blues in a considerable variety of animal tissues.

This diversity of opinion, together with the apparent absence of any actual experimental data for either side, seems to justify further study. The determination of the nature of the blue colors in feathers[3] involved the development of methods which are applicable to the identification of structural blues in other subjects, and the same criteria may be employed.

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[1] Darbishire: "Breeding and Mendelian Discovery," 41 (1911); Davenport: "Heredity in Relation to Eugenics, 27 (1911).

[2] Ann. Sci. Nat. Zool. (8) 18, (1923).

[3] Mason: J. Phys. Chem. 27, 215 (1923).

The most characteristic and most readily observed properties of the so-called "Tyndall blues" (of turbid media) are.

1. Minute particles, $< 0.6\mu$, of different refractive index from the surrounding medium.

2. Scattered light is blue; transmitted light is yellowish.

3. Scattered light more or less polarized; vibration in plane normal to the direction of the incident beam.

Other properties, such as change on swelling, permeation, pressure, etc. are applicable only when the particles are pores or cavities.

The aim of this investigation was to demonstrate either that a blue pigment was present, or that the blue was of the typical Tyndall type, analogous to the blue of the sky, smoke, skimmed milk, blue feathers, etc.

Human material was not available but the same methods may be applied to it as were employed in this study. Mr. Irvine H. Page kindly furnished us with specimens and aided in the dissection.

Several eyes of two weeks old kittens were studied. These were of a clear blue, rather better than the blue eyes of most people. (It should be mentioned that very few blue eyes are really better than a blue gray. The blues do not compare in brilliance or purity with those of the other blue media mentioned above). The material was examined within four hours of death, was not treated with any preservative, and physiological saline solution was used as a mounting medium. Observations with transmitted light were carried out with daylight, while the scattered light was observed with a dark-field illuminator, and also by sending a horizontal beam of light through the preparation in the field of the microscope, a concentrated-filament lamp and bulls-eye condenser being employed.

Polarization was observed by placing a cap nicol prism over the ocular of the microscope, and revolving this to the position of minimum intensity of the light scattered by the preparation. A selenite plate ("1st. order red") gives a red to green color change when placed below the nicol in the above system. The horizontal beam across the field of the microscope was employed for this observation. Care was taken to distinguish between effects due to the irregularities of the external surface and those due to the polarizing action within the tissue itself.

The iris was separated into the stroma layer, and the black pigment layer (uvea). The stroma, by transmitted light was turbid yellow—of the same hue as that of other turbid media; the color was not localized in pigment granules.

Against a dark ground, the stroma scatters whitish blue light and with a 3 mm objective a haze of tiny points of blue light was observed. The scattered light was partially polarized, and the vibrations were in the plane normal to the direction of the illuminating beam. No evidence of a blue pigment was noted; the yellow appearance by transmitted light would preclude the possibility of such a pigment being present.

The sclerotic layer ("white" of the eye) was of a turbid, bluish white, and microscopic study revealed the same optical characters as in the case of the iris. The absence of marked surface irregularities renders the examination simpler than that of the iris.

The pigment of the uvea is not purple but dark brownish black (melanin) and serves as a background for the turbid stroma. In like manner the choroid serves as a dark background for the sclera though the latter is frequently so thick and so opaque that the dark background is really not necessary and the sclera appears almost white.

The retina presents a bluish gray appearance, and shows the properties of a Tyndall blue medium, though to a less degree than the stroma or sclera. This is no doubt due to the scattering of light by the various minute structures of the retinal nerve endings. The "visual purple" is another thing. It is a true pigment, has been isolated and studied chemically, and it fades rapidly in the light[1].

Blue pigments appear to be very rare, except in the vegetable world, and it is probable that most blue and bluish-white turbid substances (tissues, etc.) are simply examples fo the Tyndall blue. Their nature might be established by simple tests as outlined above. It would also be interesting if some one with an abundance of experimental material would compare different shades of blue eyes and blue eyes of persons of different ages, to establish a more definite relationship between the size and number of the particles of the turbid layers and the color of the eye. A study of the increase in whiteness and opacity of the sclera with age might also be interesting.

This structural basis of the blue of eyes fits the observed fact that the blues generally become lighter and grayer with age, for a slight increase in the size of the tiny particles would accomplish this. The development of a yellow to brown pigment in the turbid stroma would of course give shades ranging from green to hazel or brown.

The conclusions of this paper confirm those of Bancroft's article[2] and are as follows:

1. In blue eyes there is no pigment in front of the uvea, which is brownish black (melanin).
2. The blue color is the color of turbid media (Tyndall blue) and is localized in the stroma.
3. The uvea serves as a dark background and permits the maximum appearance of blue from the turbid stroma.
4. Pigmentation in the stroma may combine with the blue to give green, hazel, or brown eyes.
5. Increase in the size of the particles of the turbid layer would account for lessened clearness of the blue with age.
6. The sclera consists of a thick layer of dense whitish Tyndall blue, backed by the black choroid.

Cornell University.
August 1, 1922.

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[1] Ayers: N. Y. Med. Jour. 1881, 582.

[2] J. Phys. Chem. 23, 356 (1919).

THE ELECTROLYTIC POTENTIAL OF CALCIUM

BY M. TAMELE

The electrolytic potential of calcium has not yet been determined experimentally; the value -2.5 volts (hydrogen taken as zero) usually given in tables, cannot be accepted as correct since it has been calculated from the heat of reaction[1].

The potentials of dilute lithium and calcium amalgam, as recently derived[2] seem to indicate, that calcium—contrary to expectations from the "electrochemical" theories—has the most negative potential of the alkaline earths. The values of these electrolytic potentials are of special interest since G. N. Lewis has found a curious order in the potentials of the alkali metals[3] namely, lithium, as the most negative, and then potassium, rubidium and sodium. Considering J. Heyrovský's remarks on the theory of "electro-affinity",[4] it is not improbable that the electrolytic potential of the least basigenic metal of the triad, calcium, strontium, and barium, might have the most negative value its equivalent weight being the least.

Since metallic calcium is violently attacked by all aqueous solutions, the indirect method of G. N. Lewis had to be applied, viz. to determine the potential difference between a calomel electrode and a dilute calcium amalgam in water and the potential difference between the same amalgam and the calcium electrode in a dry non-aqueous solvent, of which were tried paraldehyde, diethylamine and pyridine. However, in all of these solutions, which were carefully dried and reduced by hydrogen and kept out of contact with oxygen, calcium showed great passivity. The only way of activating the metallic calcium electrode was to scrap the surface of the metal.

After several trials, the measurements were carried out finally in the apparatus shown in Fig. 1.

In the vessel A, into which pyridine was distilled after standing twenty-four hours over metallic sodium, the electrodes B and C are placed, consisting of a calcium amalgam and a metallic calcium rod respectively. The connection to the calcium metal was made by an iron pin fixed to the lower part of the metallic rod which was fastened in a closely fitting glass tube and their connection was covered by paraffin wax.

The material used was from Kahlbaum's electrolytic calcium rod, and on analysis was found to contain traces of iron and aluminium. The amalgam was prepared by electrolysis from an aqueous solution of pure calcium chloride and was carefully dried.

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[1] N. T. Wilsmore: Z. physik. Chem. **35**, 309 (1900).

[2] J. Heyrovský: Phil. Mag. **14**, 303 (1923).

[3] G. N. Lewis and others: J. Am. Chem. Soc. **32**, 1459 (1910); **34**, 119 (1912); **35**, 340 (1913); **37**, 1983 (1915).

[4] J. Heyrovský: Proc. Roy. Soc. **102**, 628 (1923).

Close to the surface of the metallic calcium an automatic glass-scraper was fixed, which was driven by an electric motor. The electrolyte used was calcium iodide, which had been dried at 220°C in a stream of pure dry hydrogen. Dry hydrogen was passed through the solution during the measurements in order to prevent air penetrating through the bearing round the scratcher rod.

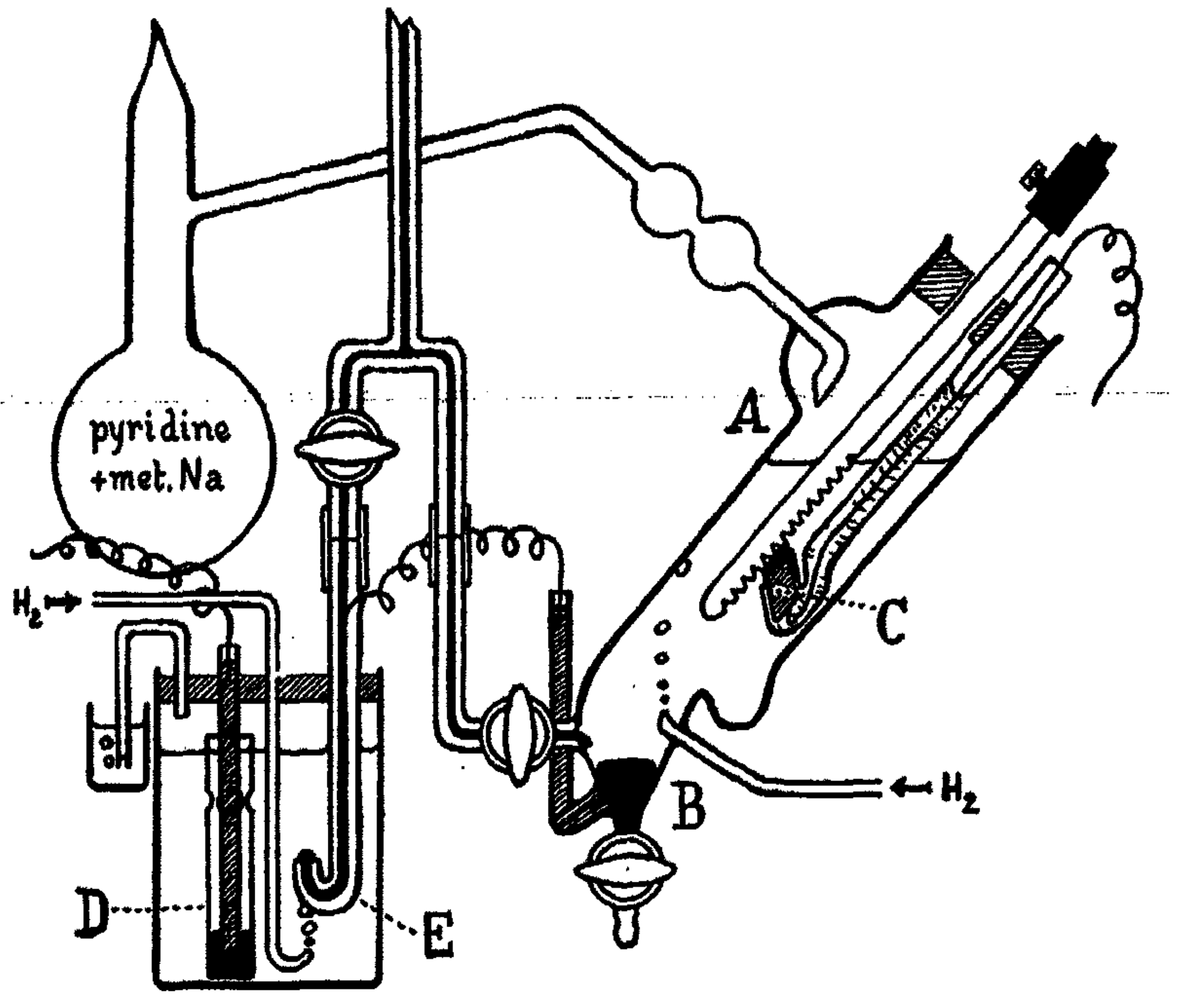

Fig 1

The aqueous cell consisted of a calomel electrode D and the calcium amalgam electrode E, which was filled with the same amalgam (from the same reservoir) as used in the pyridine cell and was occasionally renewed by allowing the amalgam to drop out slowly. The electrolyte was calcium chloride in a N/10 normal or normal solution. Pure hydrogen was also bubbled through this solution. The electrode E was connected with the electrode B by a wire and the terminals D and C of the calcium and the calomel electrodes were connected through a galvanometer to the potentiometer bridge.

The aqueous and the pyridine cell (or in some cases also a similar diethylamine cell) were first investigated separately. It has been found that the potential of the aqueous calcium amalgam electrode depends on the concentration of calcium ions as well as on the concentration of the calcium amalgam in a strictly reversible way. (See Table I).

TABLE I

Temperature 17-18°C

Amalgam	E. M. F. of the cell Amalg. | $CaCl_2$,HgClsol. | Hg.	
No. 1	N/10 $CaCl_2$	2.2765 volts
	N/100 $CaCl_2$	2.3585 volts
No. 2	N/10 $CaCl_2$	2.2765 volts
	N/100 $CaCl_2$	2.3535 volts

TABLE II

Temperature 17°-18°C

Amalgam	Concentration of the amalgam	P. D. from the N/10 calomel electrode
No. 3	0.0076%	2.2774v.
No. 4	0.0125%	2.2820v.
		0.0046v. = diff.
		calculated from the concentration ratio diff. = 0.0056 volt.

The E. M. F. of the non-aqueous cell was less constant. If not scratched the value was about 0.6 volt and indistinct. During scraping the value rose to 0.88-0.90 volts and remained constant, varying slightly with the concentration of the calcium amalgam. After prolonged, very intensive scratching the E. M. F. fluctuated towards still greater values, which was most probably due to the warming of the rubbed surface. Owing to the instability of the calcium amalgam the final determinations had to be obtained from the couple as shown in Fig. 1., to ensure the same concentration of amalgam in both amalgam electrodes.

The final results were :—

With N/1o calcium chloride in the aqueous solution the total E. M. F. = 3,120±0,005 volts; with a N/1 solution:

= 3,052 ±0,004 volts, (room temperature, 17-18°C)

These values were always obtained when not too high speeds of scratching were applied; however they coincided only within 8-10 millivolts when different electrodes were used.

From this the E. P. from the normal calomel electrode is = −3.040 and −3.048 volt or from the normal hydrogen electrode = −2.754 and −2.762 volt respectively.

Thus the electrolytic potential of calcium appears to be −2.758 ±0.004 volts, the normal hydrogen electrode being taken as zero.

The recent exact determinations of the specific heats of calcium, calcium oxide and calcium hydroxide[1] would allow us to calculate the electrolytic potential of calcium by means of the Nernst's theorem in a more exact way than that mentioned first, if the heat of oxidation of calcium were known with certainty. This is given by J. Thomsen as 131,300, by Guntz and Basset as

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[1] H. Miething: Tabellen zur Berechnung etc., Abhandl. deutsch. Bunsenges. No. 9 (1920)

151,900, by Moissan as 145,000 and by R. de Forcrand as 150,600 calories.[1]

Then the affinity A_1 of the reaction $Ca+O=CaO+Q_1$

is $A_1=RT \ln\frac{p_{o}}{p}$ where p_o = pressure of oxygen

p = partial pressure of oxygen in equilibrium with solid Ca and CaO

Further, $\log p = -\frac{Q_1}{4{,}571\,T}+1.75 \log T + \frac{\beta T}{4{,}571}+2{,}8$ (1)

For $p_0=1$, $A_1=-RT \ln p$

$$\log P = -\frac{A_1}{4{,}571\,T}$$

Hence substituting in the equation (1) we obtain

$$A_1=Q_1-4{,}571\times1{,}75T.\log T-4{,}571\times2{,}8T-\beta T^2.$$

Let us take for Q_1 the average i.e. the Moissan value as the most probable.

Then $Q_1=145{,}000$ cal.

further $T=300°$ abs.

and $\beta=-0.0017$ (from the difference of heat capacities),

whence we obtain $A_1=135{,}400$ cal.

The affinity A_2 of the reaction

$$CaO+H_2O=Ca(OH)_2+Q_2$$

using Miething's tables and taking 15,540 cal. for Q_2(Thomsen)

is $A_2=13{,}850$ cal.

To this the heat of hydration of calcium hydroxide

$$Ca(OH)_2+H_2O=Ca(OH)_2.H_2O+Q_3$$

must be added. $A_3=Q_3=2790$ cal.

Then the affinity A of the whole reaction

$$Ca+O+2H_2O=Ca(OH)_2.H_2O$$

is $A=A_1+A_2+A_3=152{,}040$ cal.

or in volts: $A=3{,}297$ volts,

which is the P. D. of the calcium electrode measured against an oxygen electrode in the saturated calcium hydroxide solution.

The P. D. of the calcium electrode against a hydrogen electrode in the same alkaline solution is 1,26 volts less.

The hydrogen electrode in this solution of hydroxide is 0,781 volt more negative, and the concentration of calcium ions in this saturated solution of hydroxide is 0,02 molar.

Thus we have $3{,}297-1{,}26+0{,}781-0{,}044=2{,}77$ volts, which is the P. D. between the normal calcium electrode and the normal hydrogen electrode and should be equal to the normal electrolytic potential of calcium, which has been found to be 2,76 volts.

The author is much obliged to Professors B. Brauner and J. Heyrovský for their encouragement and help.

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of the Charles University, Prague.

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[1] J. W. Mellor: Treatise on Inorg. and Theor. Chem. 3, 662 (1923).

FLUOSILICIC ACID. III: METHOD OF TITRATING AND PROPERTIES

BY C. A. JACOBSON

In previous communications[1] the author has reported upon the preparation of fluosilicic acid having a concentration in water solution of nearly 61%, which he considers the maximum obtainable at room temperature. He has also shown by several different types of experiments that this acid does not exist as such in the vapor phase, but decomposes into SiF_4 and H_2F_2 the moment it passes out of liquid water, and is similar to carbonic and sulfurous acids in this respect. It has also been shown that when the acid is thus decomposed the silicon tetrafluoride formed may exist in the presence of water vapor without combining with it to precipitate fluosilicic acid and silicic acid or silicon dioxide; and, whenever hydrofluoric acid reacts with silicon dioxide or glass in the presence of water, the SiF_4 first formed immediately reacts with the water to form fluosilicic and silicic acids according to the equation:

$$3SiF_4+4H_2O=2H_2SiF_6+H_4SiO_4$$

From the fact that so many different methods for the quantitative determination of this acid in solution have been proposed one may rightly infer that the determination is fraught with many difficulties. Other acids like hydrofluoric and hydrochloric may accompany it except when especially purified, so that when the fluosilicic acid is determined volumetrically the results will be too high. Various methods have been recommended to circumvent the difficulty but none are entirely satisfactory.

Katz[2] suggests first to titrate the H_2F_2 and one third of the H_2SiF_6 in 50% alcohol, and then the remaining two thirds of the latter acid in water, using normal alkali, but found that the first stage titration was indefinite on account of the color of the indicator fading out more or less rapidly. Others have tried to precipitate the hydrofluoric acid as insoluble fluorides and then titrating the remaining fluosilicic acid, but these methods have also been discarded for the reason that insoluble fluosilicates are formed together with the fluorides.

S. Hönig[3] has taken a long step forward in working out a satisfactory method by suggesting that the acid can be titrated in two stages, but did not follow up his preliminary work until a really satisfactory method was evolved. It is along this line that the author has expended most of his energies, and now believes that he has a method, though not yet perfect, may be considered an improvement over the older methods. The principles of this method were first suggested to him by the late Dr. B. F. Lovelace of Johns Hopkins University, although the essential details have been worked out independently.

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[1] J. Phys. Chem. 27, 577, 761 (1923).

[2] Chem. Z. 28, 356, (1904).

[3] Chem. Z. 31, 1207.

The method consists in adding a suitable neutral salt which reacts with the acid and precipitates the insoluble fluosilicate, allowing of two independent titrations of the original portion of acid, thus letting one serve as a check upon the other. A volume of the water solution of the acid, not exceeding 10 cc, and containing not over 0.1-0.2g. H_2SiF_6 is cooled in an ice-bath to approximately zero degrees. To this solution is added about a gram of KCl or NaCl, and it is then titrated with one normal alkali, using methyl orange as indicator. A sharp end-point is obtained. The reactions that take place may be represented as follows:

$$H_2SiF_6+2KCl=K_2SiF_6+2HCl$$
$$2HCl+2KOH=2KCl+2H_2O$$

This is the first stage of the titration and gives uniform results provided no other acid is present, in which case the results would be too high. Water is then added to the titration mixture until the volume amounts to 50-75 cc, but not in excess of the latter volume, and heated to near boiling, (95°). About 5 drops of a phenolphthalein solution are added and the solution titrated to color while near the boiling point. The methyl orange first added does not interfere with the detection of the end-point in the second stage. The reaction taking place in this stage may be represented thus:

$$K_2SiF_6+4KOH=6KF+H_4SiO_4$$

where it is seen that twice as much alkali is required in the second titration as in the first. One titration therefore serves as a check upon the other, but a small correction must be applied to the second stage, which is negative and amounts to about 0.6% for an acid titrating 30-50% by the first stage.

While this method for determining H_2SiF_6 seems to yield more consistent results than the others, it is by no means perfect. The two principal imperfections may be given as follows: It is very difficult to maintain the temperature so low and the solution so concentrated that the reaction products of the first stage will not begin to pass over into the second before the first-stage reactions are completed. The temperature should therefore be kept as near zero as possible and the concentration of acid not less than one or two percent, while the actual amount of acid titrated should be small. The last-mentioned condition will prevent the dilution of the solution with a large volume of the base and cause an appreciable temperature rise due to the heat of reaction. When these conditions are not fulfilled there will be a more or less gradual fading of the indicator due to the products of the reaction passing into the second stage, which is more pronounced the higher the temperature and the more dilute the solution. Hudleston and Bassett[1] have carried out an elaborate investigation of these fading phenomena, but all their data seem to support the view that the fluosilicate goes over to the fluoride and silicic acid in the presence of alkali, and that this transformation is accelerated by temperature and dilution. Their fading experiments, therefore, seem to have but minor significance.

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[1] J. Chem. Soc. 119, 405 (1921)

The other imperfection in the method applies to the second-stage titration where slightly higher results are obtained than demanded by theory, and therefore a negative correction must be applied to the results in this stage. No satisfactory explanation of this is at hand, but it may be due, at least in part, to the adsorption of free acid by the precipitated fluosilicate, which is removed from the sphere of action in the first stage but liberated and titrated when the salt is decomposed. Another, and more plausible explanation may be found in the fact that strong alkalis attack glass and various silicates. The

TABLE I

Exp.	Vol. titrated	Temp.	1g. Salt	Indicator	cc. N NaOH	%H_2SiF_6	Correction
1	10 cc.	10°	NaCl	Me-Or	9.91	35.76	
	60 cc.	95°		Ph-th	29.95	36.02	−0.26
2	10 cc.	10°	NaCl	Me-Or	7.21	52.03	
	60 cc.	95°		Ph-th	21.98	52.87	−0.84
3	10 cc.	10°	NaCl	Me-Or	8.01	57.80	
	60 cc.	95°		Ph-th	24.34	58.34	−0.74
4	10 cc.	10°	KCl	Me-Or	3.47	37.56	
	60 cc.	95°		Ph-th	10.58	38.17	−0.61
5	10 cc.	10°	KCl	Me-Or	2.43	26.29	
	60°	95°		Ph-th	7.43	26.81	−0.52
6	10 cc.	10°	KCl	Me-Or	7.50	54.15	
	60 cc.	95°		Ph-th	15.19	54.79	−0.64
7	10 cc.	10	KCl	Me-Or	7.56	54.55	
	60 cc.	95		Ph-th	15.35	55.38	−0.83
8	10 cc.	10	KCl	Me-Or	7.75	55.92	
	60 cc.	95		Ph-th	15.68	56.58	−0.66
9	10 cc.	10	KCl	Me-Or	7.66	55.29	
	60 cc.	95		Ph-th	15.39	55.51	−0.22
10	10 cc.	10	KCl	Ph-th	7.55	54.48	
	60 cc.	95		Ph-th	15.40	55.56	−1.08
11	60 cc.	10	KCl	Ph-th	7.70	55.56	
	60 cc.	95		Ph-th	15.31	55.24	+.32
12	60 cc.	10	KCl	Ph-th	7.02	33.77	
	60 cc.	95		Ph-th	20.74	33.26	+.51

silicic acid, which is formed in the second stage titration, being slightly soluble in hot water, would undoubtedly react with the alkali to form the soluble ortho or meta silicate. Consequently, the larger the volume of water used in the second-stage titration the greater would be this influence. This assumption has been verified by a long series of experiments. The volume of liquid in the second stage titration was gradually increased from 25 cc to 1000 cc, and the results found to increase in the same ratio as the volume, so that when the original 10 cc liquid in the first stage was diluted to one liter and titrated in the second stage the results were about 4.5% higher than by the first stage titration, that is, for a 55% H_2SiF_6 solution. Further consideration will be given to this problem.

Table I contains a few actual readings, illustrative of the method.

Column 1 of the table gives the number of the experiment carried out in two stages. Column 2 gives the volume of the acid titrated, 3 the temperatures, 4 the neutral salt added, 5 the indicator, as explained in the note, 6 the number of cc of normal NaOH used for titration, 7 the percentage of acid found and 8 the correction to be applied to the second-stage titration. Methyl orange is abbreviated to Me-Or and phenolphthalein to Ph-th in column 5.

From the first eight experiments, performed under similar conditions, it is seen that the average correction to be applied to the second stage titration is −.64% when acids analyzing between 26% and 58% are titrated. The ninth brings out the influence of dilution on the first-stage titration where it is seen that the first-stage reaction has been slightly exceeded, and in the tenth the influence of the indicator. Experiments 11 and 12 show that when the same volume of acid is used in the first and second stage together with phenolphthalein as indicator in both stages, the first-stage titration is slightly higher than the second. Experiment number eight was titrated with a 0.6628N KOH instead of a normal solution as the others. It is seen that the more dilute alkali increases the titration value of the acid about 2%, due in all probability to the solubility and titration value of the resulting silicic acid.

Properties of the acid. Fluosilicic acid is a non-volatile acid, and as far as we know, existing only in water solution. It can be concentrated at room temperature to approximately 61%. At this concentration the solution has a distinct odor, due to the decomposition products of the acid. It has a sharp stinging taste which in dilute solution is suggestive of alum. The specific gravity of a 60.79% solution at 25° was found to be 1.4634, and the index of refraction at the same concentration and temperature 1.3465. In dilute water solution the acid is quite stable, for it may be kept in glass vessels for a long period of time without etching, and the etching that eventually takes place is found right above the surface of the liquid. Whereas the acid was formerly supplied at a concentration not much above 20%, it can now be purchased at concentrations well above 50%. Some work has been done to determine the value of other indicators and neutral salts upon the two-stage titration of this acid; but the investigations are not far enough advanced to warrant a report at this time.

Morgantown, W. Va.
September 8, 1923.

THE FORMATION OF PHOSPHORUS PENTACHLORIDE FROM PHOSPHORUS TRICHLORIDE AND CHLORINE[1]

BY H. AUSTIN TAYLOR

The results of recent work[2] on gas reactions have led to the conclusion that nearly all chemical reactions are catalytic in nature, whether they are catalysed by the surface of the containing vessel or by the water present in the majority of reaction systems. The earlier ideas of the general stability of molecules have to be modified in view of the great influence of polar substances on various reactions, and at the same time, the number of gaseous bimolecular reactions which are now known to occur in the gas phase without a catalyst in any form, is rapidly decreasing. It is of interest therefore to investigate some of the more well-known reactions which are at present assumed to be straight bimolecular reactions.

An attempt has been made in this work to show that the formation of phosphorus pentachloride from the trichloride and chlorine is actually an uncatalysed reaction occurring in the gas phase and in absence of water vapour. The known properties of phosphorus trichloride and its general reactivity would lead one to expect that it required a very small amount of activation, if at all, and hence would probably react in the gaseous state.

At the outset the intention was to see if there was any difference between the amounts of phosphorus pentachloride which formed on a typical polar surface, glass, and on a typical non-polar surface such as paraffin wax, when the mixed vapours of phosphorus trichloride and chlorine were passed over both for the same length of time. With this end in view, a vessel was moulded in paraffin wax, Norrish having shown that on coating a glass vessel with wax the cracks in the latter offered sufficient glass surface for the reaction to proceed to some extent. The vessel consisted of a reaction chamber of approximately 100 cubic centimetres capacity, carrying at one end two side-tubes entering in opposite directions through which the trichloride and chlorine vapours respectively could be passed. At the other end of the wax vessel was a third tube as outlet for remaining gases. The third tube was sealed to a glass reaction chamber by melting the wax tube, so that the gases before finally leaving the apparatus passed first over the wax surface and then over the glass.

The phosphorus trichloride was purified by distillation and boiled at 75.9°C. Chlorine was prepared by the action of hydrochloric acid on potassium permanganate, was washed free from any hydrochloric acid by passing through two gas washers containing water and dried by two gas washers containing sulphuric acid and finally over phosphorus pentoxide in a tube about 30 cm. in length. The resulting dry chlorine was liquefied in a spiral

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[1] Contribution from the Laboratory of Physical Chemistry. Princeton University.

[2] *Inter alia.* Norrish: J. Chem. Soc., 123, 3006 (1923).

gas bubbler immersed in a freezing mixture of solid carbon dioxide and ether. The phosphorus trichloride was placed in a similar spiral bubbler, maintained at room temperature and attached directly to one arm of the reaction chamber, the other arm being waxed to the chlorine holder.

In this way the vapours of the two liquids could be mixed in the wax vessel by passing dry nitrogen through both bubblers, since the vapour pressures of both liquids are quite appreciable under the conditions cited. The nitrogen used was drawn from a cylinder of the compressed gas and passed successively through a drying tube of phosphorus pentoxide and a U tube containing glass wool, immersed in liquid air, to freeze out remaining traces of water vapour. By means of a by-pass (which was later sealed) in the chlorine bubbler, dry nitrogen, or nitrogen with some phosphorus trichloride vapour, could be passed through the whole apparatus, by first solidifying the chlorine temporarily in liquid air. Passing dry nitrogen in this manner through the whole apparatus for a period of twenty-four hours whilst repeatedly heating the glass portions which were made of pyrex, the residual water on the surfaces could be more efficiently removed. The wax vessel on the other hand was subjected to a stream of nitrogen and phosphorus trichloride vapour for the same length of time. The small amount of water present may be assumed to react with the trichloride to give the solid phosphorus oxychloride POCl which itself possesses an appreciable vapour pressure at ordinary temperatures and would thus volatilise away. It is reasonably certain that, in this way the reaction system was dry: more certain is it that conditions were drier than held in the reaction studied by Norrish between ethylene and bromine, where water vapour was assumed absent.

The first test was then made, by liquefying the chlorine again in carbon dioxide snow, and passing nitrogen through both liquids as described above. After a period of an hour and a half when a reasonable amount of the pentachloride was visible in the glass vessel the two reaction chambers were detached and weighed separately. Dry air was then blown through each to volatilise the phosphorus pentachloride and the empty vessels reweighed. The difference between the two weighings gave the amount of pentachloride in each of the two vessels. It was found that, the wax vessel contained 3.810g. whilst the glass vessel contained only 0.384g. That is, the reaction had apparently taken place almost entirely in the wax vessel. The reaction therefore appeared to be independent of the containing surface the presence of phosphorus pentachloride in the glass vessel being due to reaction between some molecules which had not reacted in the wax vessel, or to condensation in the glass vessel from the vapour phase.

That such was actually the case was shown by replacing the wax vessel by an almost identical one of glass and repeating the experiment. Connections between the two glass reaction chambers was made with paraffin wax, and the same drying process observed as previously. It was found finally that after passing the gases for half an hour[1] the first glass vessel which replaced the wax one used previously contained 0.69g. of phosphorus pentachloride whilst only 0.039g., formed in the second.

Although no comparison can be made between the amounts of phosphorus pentachloride formed in a given time in both the wax and glass vessels owing to the difference in rates of nitrogen flow in the two cases, nevertheless the second result substantiates the fact that the major part of the reaction occurs when the vapours first mix, that is in the first reaction chamber, and since the polarity of the surface is apparently negligible the reaction must occur in the gaseous phase.

If this view is correct the reaction ought to be visible owing to the formation of phosphorus pentachloride as a cloud. To test this, the two vapours in dry nitrogen were made to impinge on one another in a three litre flask. It was observed that immediately the gases were admitted to the flask a small amount of phosphorus pentachloride formed as a film on the glass and after a delay of 20 or 30 seconds the whole flask was suddenly filled with a white cloud which was composed of quite large particles of phosphorus pentachloride resembling fine snow flakes, which dropped to the bottom of the flask; the continued reaction occurred, still as a cloud, but of a much finer texture and thinner, being at times scarcely visible. The whole phenomenon resembled the precipitation of a supersaturated vapour, since it was further noticed that the cloud formation was initiated in the region where the first film of phosphorus pentachloride had formed, and travelled from there in a direction opposed to the normal direction of flow of the gases, towards the point at which the gases first impinged on one another. The reason for this would appear to be, that the supersaturated vapour of phosphorus pentachloride formed where the phosphorus trichloride and chlorine impinged, spread under the force of the nitrogen stream towards the phosphorus pentachloride film on the flask, where precipitation was caused by particles of solid phosphorus pentachloride, the precipitation then travelling back throughout the whole supersaturated vapour. Succeeding reaction between phosphorus trichloride and chlorine would not show such a definite cloud formation as initially, since the numerous phosphorus pentachloride particles throughout the flask would prohibit the formation of further supersaturated vapour, precipitating it as formed.

The rigorous process of drying adopted in the first experiments quoted, was not observed with the flask later employed, save that dry nitrogen and phosphorus trichloride were blown through it for a short time before the chlorine was admitted. Two possible explanations remain to be excluded, namely that dust particles, or water act as catalysts in the case of the cloud formation.

The first experiments would exclude the possibility of water vapour acting as a catalyst, since phosphorus pentachloride was formed in its absence,

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[1] It was noticed in this second case that phosphorus pentachloride had begun to drop from the first chamber into the second, and it seemed advisable to stop the experiment even after this short period.

whilst the delay before the actual formation of the cloud would assist in the removal of traces of water by the phosphorus pentachloride first formed, the cloud then forming in a dry atmosphere. However, on introducing water intentionally by passing the chlorine vapours through water before mixing with the phosphorus trichloride it was found that the formation of a cloud was completely inhibited, the only evidence of reaction being the film on the walls of the vessel. Nor was it possible to produce the cloud again until the flask had been once more dried. Baker[1], after repeated failures, succeeded once in obtaining a vapour density of phosphorus pentachloride greater than that for complete dissociation. This ill success even after vigorous drying indicates that water has little influence in the opposed reaction and therefore confirms the above conclusion.

With regard to dust particles, the delay in cloud formation would also seem to preclude this possibility. The manner of propagation would also indicate the absence of effect due to dust particles since we can only assume that the dust particles are as likely to be situated in one spot as another.

The course of the cloud formation as previously observed was confirmed by passing the gases, both in the same direction down a horizontal glass tube, two metres long and seventy five millimetres in diameter. A thin film of phosphorus pentachloride was first observed on the tube fifteen centimetres away from the inlet tubes, spreading slowly down the lower half of the tube throughout its whole length. After a period of about a minute a cloud started and spread thence in both directions namely back towards the inlet tubes and also down the tube in the normal direction of the gas flow

It would appear therefore, that the explanation of the cloud formation offered above, namely by some phosphorus pentachloride which had already condensed on the glass surface, was true. From this it can only be concluded that the reaction between phosphorus trichloride and chlorine to give phosphorus pentachloride is a gas reaction at ordinary temperatures occurring in the gas phase and unaffected by catalysts.

The speed of the reaction under the conditions cited precludes the evaluation of the rate of combination. It has been shown that liquid chlorine and phosphorus trichloride react violently at 87 — °C.

Summary

1. Dry phosphorus trichloride and chlorine vapours in dry nitrogen react as completely in a wax vessel as in a glass one.

2. The phosphorus pentachloride formed gives rise to an easily supersaturated vapour which is precipitated as a white cloud by some phosphorus pentachloride condensed on the containing vessel.

3. The reaction is a true gaseous reaction being unaffected by surface catalysts as also by water.

In conclusion I desire to thank Professor H. S. Taylor at whose suggestion the problem was investigated and for advice and assistance during its progress.

Princeton, N. J.

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[1] J. Chem. Soc., 77, 648 (1900).

NEW BOOKS

Valence. *By G. N. Lewis. 23×16 cm; pp. 172. New York: The Chemical Catalog Company, 1923. Price: $3.00.* In the preface the author says that "to attempt to keep pace with the rapid development in so many ramifications of science, all of which contribute to our knowledge of the atom and molecule, is, especially for one who is at best a slothful reader, an impossible task. Nevertheless it is the same atom and the same molecule that is being studied by the organic chemist, the inorganic chemist, and the physicist; the marvellously exact conclusions of the spectroscopist, the far more vague, but equally difficult and important generalizations of the student of the carbon compounds, must contribute, each in due measure, to our knowledge of that microcosmos, which appears to us the more mysterious as its nature becomes more nearly revealed to us. It was with this thought in mind that I have devoted several of the earlier chapters to an attempt to bring to the better acquaintance of chemists some of the astounding accomplishments of modern physics."

The chapters are entitled: the atomic theory; the periodic law and the chemist's picture of the atom; spectral series and the physicist's view of the atom; reconciliation of the two views—the arrangement of electrons in the atom; the union of atoms—the modern dualistic theory; the new theory of valence—the chemical bond; double and triple bonds; exceptions to the rule of eight; valence and coordination number; compounds of elements with small kernels; elements of positive and negative states; remnants of the electrochemical theory; the source of chemical affinity—a magnetochemical theory; the discontinuity of physico-chemical processes.

"It is singular that so many years elapsed after the announcement of Faraday's law before it was realized that this law implies a discontinuity of electricity in the same degree that Dalton's law implied a discontinuous structure of ordinary matter. By the same reasoning electricity occurs in quanta that are all alike, and capable of combining with atoms and groups of atoms only by integral numbers. It was Helmholtz in his celebrated Faraday lecture of 1881 who first pointed out this deduction of the atom of electricity, or as it is now called, the electron. Our knowledge of the atom of negative electricity, the electron, is largely due to the brilliant investigations of J. J. Thomson and of those whom he has inspired. The proof that free electricity is negative electricity; the determination of the ratio between the charge and the mass of an electron; and the study of the physical and chemical effects produced by moving electrons, comprise one of the most fascinating chapters of modern science.

"The study of saline substances was greatly fostered by the electrolytic dissociation theory of Arrhenius (1887) which clarified in so remarkable a manner our ideas concerning salt solutions. This theory through a generation of criticism has fully justified its essential accuracy. We are fully convinced that, in a dilute aqueous solution of sodium chloride, this salt is separated into two distinct parts, one of which has a negative charge, equal to the charge of an electron, while the other is positively charged in equal amount. Thus we have full demonstration of a phenomenon which was assumed in the dualistic theory.

"Again chemists were tempted to revert to the electrochemical theory as an explanation of all chemical union, and again they met the difficulty of explaining by such means the properties of substances like methane and diatomic hydrogen. There obviously is a wide gap between extreme types; on the one hand an extremely 'polar' substance like sodium chloride, in which presumably there is at all times a considerable displacement of electricity from the sodium to the chlorine, and which sometimes completely dissociates into sodium and chloride ions; on the other hand a relatively non-polar substance like diatomic hydrogen which gives no *a priori* reason for, nor shows any evidence of, such electric displacement. Must we conclude that there are two distinct types of chemical union, one a completely polar and the other a completely non-polar type, and must we assume that a substance which appears to have intermediate properties, and to be slightly polarized electrically, is merely a mixture of polar and non-polar molecules? Or can we find some means of ascribing all the most varied types of chemical union to one and the same fundamental cause, differing only in the nature and degree of its manifestation? These are questions which will occupy our attention in later chapters," p. 21.

"It was Rydberg (1897, 1914) who first comprehended the underlying truth in the periodic classification. The properties of an element are determined by a single 'independent variable' which is not, however, the atomic weight. In the second of his remarkable papers in which Rydberg gave the ordinal number of each element, he was obliged to decide upon the exact placing of all the elements of the rare earths, upon the number of elements still remaining undiscovered, and upon the exact position of these vacancies in the periodic table. In all of these difficult tasks he was completely successful, and his table of ordinal numbers is identical with our present table of atomic numbers, except that he assumed the existence of two elements between hydrogen and helium. If we reduce all his numbers, except the first, by two we obtain the accompanying table, which gives the atomic numbers that are now adopted," p. 24.

"Now Rydberg was unquestionably wrong in assuming the two atomic numbers between those of hydrogen and helium. This seems to be entirely demonstrated by the relations between the spectrum of hydrogen and the enhanced spectrum of helium, which we shall discuss in the next chapter. Moreover, although only a few members of the last period of the elements are known, the first part of this period does not seem to be analogous to the period of 32 just preceding, but rather shows great resemblance to the period before that, which is one of 18. Thus thorium is more like zirconium than like cerium, while uranium, the sixth member of the last period, belongs definitely in the same family as molybdenum (which is the sixth member of the last period of 18) and seems to bear no resemblance to neodymium (which is the sixth member of the period of 32). While therefore the facts do not substantiate Rydberg's theory in full, nevertheless we shall see later that his series of quadratic numbers plays an important rôle in our present theory of economic structure," p. 27.

"In his later work Bohr entirely abandoned the ring of electrons. He found that even the phenomena of spectral lines in the visible and in the X-ray regions could not be interpreted in terms of a theory which regards the electrons as associated with one another in joint orbits. He now assigns to each electron its separate orbit and regards these orbits as situated about the atomic center in shells. It seems to me that by this step Bohr has removed every essential element of conflict between the views of the physicist and the chemist. If we regard as the important thing the orbit as a whole, and not the position of the electron within the orbit, and if each electron is assigned an independent orbit, then we may think of each electron orbit as having a fixed position in space. The average position of the electron in the orbit may be called the position of the electron and will correspond entirely to that fixed position which was assigned in the theory of the static atom.

"Let us therefore now attempt to weld these different views into a single theory of atomic structure which, while it certainly can claim no degree of finality, will summarize all of the evidence, chemical and physical, which we now possess regarding atomic structure.

"1. First we shall adopt the whole of Bohr's theory in so far as it pertains to a single atom which possesses a single electron. There are no facts of chemistry which are opposed to this part of the theory, and we thus incorporate in the new model all of the Bohr theory that is strictly quantitative.

"2. In the case of systems containing more than one nucleus or more than one electron, we shall also assume that the electron possesses orbital motion, for such motion seems to be required to account for the phenomenon of magnetism; and each electron in its orbital motion may be regarded as the equivalent of an elementary magnet or magneton. However, in the case of these complex atoms and molecules we shall not assume that an atomic nucleus is necessarily the center or focus of the orbits.

"3. These orbits occupy fixed positions with respect to one another and to the nuclei. When we speak of the position of an electron, we shall refer to the position of the orbit as a whole rather than to the position of the electron with the orbit. With this interpretation, we may state that the change of an electron from one position to another is always accompanied by a finite change of energy. When the positions are such that no change in position of the several parts of the atom or molecule will set free energy, we may say that the system is in the most stable state.

"4. In a process, which consists merely in the fall of an electron from one position to another more stable position, monochromatic radiant energy is emitted, and the frequency of this radiation multiplied by h, the Planck constant, is equal to the difference in the energy of the system between two states.

"5. The electrons of an atom are arranged about the nucleus in concentric shells. The electrons of the outermost shell are spoken of as valence electrons. The valence shell of a free (uncombined) atom never contains more than *eight electrons*. The remainder of the atom, which includes the nucleus and the inner shells, is called the kernel. In the case of the noble gases it is customary to consider that there is no valence shell and that the whole atom is the kernel.

"6. In my paper on "The Atom and the Molecule" I laid much stress upon the phenomenon of the pairing of electrons. I have since become convinced that this phenomenon is of even greater significance than I then supposed, and that it occurs not only in the valence shell but also within the kernel, and even in the interior of the nucleus itself. It has not seemed desirable to discuss in this book the extremely interesting modern ideas concerning the structure of the atomic nucleus, but if we adopt the old hypothesis of Prout it is possible from the atomic weight and the atomic number alone to determine the number of hydrogen nuclei and the number of electrons which compose the nucleus of a given atom. It is a striking fact that with very few exceptions the number of nuclear electrons so calculated is an even number. It is furthermore to be noted that whenever a radioactive atom emits one beta-particle it almost immediately emits another, again illustrating the instability of an unpaired electron within the nucleus. So also we find that in all the more stable states which atoms assume, the electrons occur in even numbers in the several inner shells. Later we shall show that the valence electrons almost invariably follow the same rule. The simplest explanation of these facts appears to lie in the assumption of a physical pairing of the electrons. There is nothing in the known laws of electric force, nor is there anything in the quantum theory of atomic structure, as far as it has yet been developed, to account for such pairing. However we have seen that an electron within the atom must be regarded as a magnet and two such magnets, would tend to be drawn together. While the classical theory of magnetism would hardly suffice to account fully for this phenomenon of pairing, there can be no question that the coupling of electrons is intimately connected with the magnetic properties of the electron orbits, and the explanation of this phenomenon must be regarded as one of the most important outstanding problems in quantum theory.

"7. We may next consider a very recent idea advanced by Bohr (1921), which is not based so much upon deductions from his atomic model as upon a direct consideration of the experimental data on spectral series. He assumes essentially that the first shell is associated with a single energy level, and that this level can accommodate one pair of electrons, that the second shell contains two energy levels, each of which is capable of holding two pairs of electrons, making a maximum of eight electrons in the second shell. The third shell has three energy levels, each of which can hold three pairs of electrons, so that the maximum number of electrons in the third shell is eighteen. The fourth shell comprises four levels, each capable of holding four electron pairs, making a total of thirty-two electrons, and so on. We shall see the great utility of this conception as we now proceed to consider the arrangement of electrons in the various elements," p. 56.

"Many years ago I was led to the conclusion that when we speak of an element of variable valence we are including two very different types of phenomena, and that such a change as the oxidation of hydrogen sulfide to sulfurous or sulfuric acid is a very different kind of change from the one which occurs when a ferrous salt is converted into a ferric, or a titanous salt into a titantic. There are numerous reasons for suspecting a fundamental difference between these two types of oxidation. For example, in the first type oxidation and reduction usually occur by steps of two, while the second type more often involves a change of but one step. Substances which undergo the second type of change are usually colored, while those involved in the first type of change are usually colorless. The distinction between the two types was expressed in my paper of 1916 by referring to the atoms which undergo the second type of valence-change as *atoms of variable kernel.*

"The properties of the various elements which come before titanium are in accord with the assumption that the electrons which are a part of the kernel do not take part in chemical reactions, but as we now proceed to elements of higher atomic number we shall see that this simple rule is by no means universally valid," p.60.

"The great success of structural organic chemistry led to attempts to treat inorganic compounds in a similar manner, not always happily. I still have poignant remembrance of the distress which I and many others suffered some thirty years ago in a class in elementary chemistry, where we were obliged to memorize structural formulae of a great number of inorganic compounds. Even such substances as the ferricyanides and ferrocyanides were forced into the system, and bonds were drawn between the several atoms to comply with certain artificial rules, regardless of all chemical evidence. Such formulae are now believed to be almost, if not entirely, devoid of scientific significance.

"Such abuse of the structural formula inevitably led to a reaction which found its best expression in the publication of Werner. His "*Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*" (1905) marked a new epoch in chemistry; and in attempting to clarify the fundamental ideas of valence, there is no work to which I feel so much personal indebtedness as to this of Werner's. While some of his theoretical conclusions have not proved convincing, he marshalled in a masterly manner a great array of facts which showed the incongruities into which chemists had been led by the existing structural formulae of inorganic chemistry," p.67.

"It is customary in works on inorganic chemistry to call ferric iron trivalent and ferrous iron bivalent. Now this phraseology is not only out of harmony with that of organic chemistry, but it is essentially bad in that it gives a number without a sign. Thus nitrogen would be said to be trivalent both in ammonia and in nitrous acid. In all cases where the polar number is to be indicated I propose a slightly different mode of expression. Let us say that nitrogen in ammonia is *trinegative*, and that it is *tripositive* in nitrous acid. So also let us say that iron is tripositive in ferric salts and bipositive in ferrous salts," p. 70.

"We have already noted the preponderating tendency of every atom toward an arrangement of electrons with eight in the outermost shell. This arrangement of outer electrons, which Parson and I called the "group of eight", and which has since been tersely expressed by Langmuir as the "octet", is attained when atoms lose or gain electrons to form ions.

"So when calcium and chlorine unite, the calcium atom by giving off two electrons, and each chlorine atom by acquiring one electron, assume the ionic state in which each atom has the group of eight in its outermost shell. However, we have seen that the assumption of such ionizations as a necessary accompaniment to all chemical combinations, even if it is assumed to be only "intramolecular" ionization, leads to conclusions which are not reconcilable with the facts of chemistry.

"The new theory, *which includes the possibility of complete ionization as a special case*, may be given definite expression as follows: Two atoms may conform to the rule of eight, or the octet rule, not only by the transfer of electrons from one atom to another, but also by sharing one or more pairs of electrons. These electrons which are held in common by two atoms may be considered to belong to the outer shells of both atoms.

"The discovery that those electrons which are held jointly by two atoms always occur in pairs led to the realization that the "rule of two" is even more fundamental than the "rule of eight". We see at the beginning of the periodic table that helium with its pair of electrons has the same qualities of stability that characterize the remaining rare gases which possess outer octets. Hydrogen may form hydrogen ion with no electrons, it may form hydride ion by adding one electron and thus completing the stable pair, or finally two hydrogen atoms may unite to form the hydrogen molecule, in which each atom shares with the other this stable pair of electrons.

"I called particular attention to the remarkable fact that when we count up the electrons which are comprised in the valence shells of various types of molecules, we find that of some hundred thousand known substances all but a handful contain an even number of such electrons. It is therefore an almost universal rule that the number of valence electrons in a molecule is a multiple of two.

"Certain metallic vapors which are produced at high temperatures are exceptions to this rule. Other exceptions which are found at high temperatures are the monatomic forms of hydrogen and the halogens, while at ordinary temperatures we have nitric oxide, nitrogen dioxide and chlorine dioxide, with 11, 17, and 19 valence electrons," p. 79.

The author's attitude toward Langmuir is worth noting, p. 87. "In my original paper I contented myself with a brief description of the main results of the theory, intending at a later time to present in a more detailed manner the various facts of chemistry which made necessary these radical departures from the older valence theory. This plan, however, was interrupted by the exigencies of war, and in the meantime the task performed, with far greater success than I could have achieved, by Dr. Irving Langmuir in a brilliant series of some twelve articles, and in a large number of lectures given in this country and abroad. It is largely through these papers and addresses that the theory has received the wide attention of scientists.

"It has been a cause of much satisfaction to me to find that in the course of this series of applications of the new theory, conducted with the greatest acumen, Dr. Langmuir has not been obliged to change the theory that I advanced. Here and there he has been tempted to regard certain rules or tendencies as more universal in their scope than I considered them in my paper, or than I now consider them, but these questions we shall have a later opportunity to discuss. The theory has been designated in some quarters as the Lewis-Langmuir theory, which would imply some sort of collaboration. As a matter of fact Dr. Langmuir's work has been entirely independent, and such additions as he has made to what was stated or implied in my paper should be credited to him alone."

"It seems to me that the most important addition to my theory of valence lies in the suggestion of what has become known as the hydrogen bond. The idea was first suggested by Dr. M. L. Huggins, and was also advanced by Latimer and Rodebush, who showed the great value of the idea in their paper to which reference has already been made.

"This suggestion is that an atom of hydrogen may at times be attached to two electron pairs of two different atoms, thus acting as a loose bond between these atoms. Thus it is assumed that two molecules of water may unite as follows: $\mathrm{H}:\underset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}}:\mathrm{H}:\underset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}}:$. The atom of hydrogen attached to the two oxygen atoms represents the new type of bond. This theory of the hydrogen bond offers an immediate explanation of a large number of complexes involving water, ammonia and other such compounds, which have hitherto been inexplicable by any kind of structural formula," p.100.

"In liquids, especially of the 'sticky' kind, and in glasses, the simple molecules which exist in the gaseous state presumably become attached to one another and often form chains or groups in which the individuality of the simple molecule is partly or wholly lost. Such groups or continuing molecules, probably have an extent which is determined by adventitious circumstances. On the other hand in crystalline substances these continuing molecules may be conceived as coterminous with the complete crystal, and characterized by a well-ordered arrangement, except where the crystal is distorted or broken," p. 116.

"Attempts to apply quantum theory to chemical reactions have been largely limited to a study of reactions produced by light and of the light set free by chemical reactions. It has long been known that numerous photochemical reactions which occur in the presence of blue or violet light occur to a far more limited extent or not at all in red light. So also reactions which are not produced by visible light take place upon exposure to ultraviolet radiation.

"If one or more of the reacting molecules must receive a certain quantity of energy before it can react, then we should expect from quantum theory that no exposure to radiation, no matter how protracted, would cause the reaction to occur, unless the frequency of the radiation were high enough to make $h\nu$ as large as the energy required by the reacting molecule. It is true no case is known of a typical photochemical reaction which occurs rapidly with light of a given frequency and which does not occur at all with light of a little lower frequency. Nor perhaps is this ordinarily to be expected, since different molecules, owing to thermal agitation, would require somewhat different amounts of energy to reach a condition in which they would react.

"The interesting idea has been suggested by W. C. McC. Lewis (1916) and by Perrin (1919) that all chemical reactions are photochemical in character. They assume that a molecule does not react until it becomes activated by radiant energy of a certain minimum frequency. This light may come from outside the system, as in the typical photochemical process, or it may exist in the interior of the reacting system as thermal radiation. The relative content of high frequency radiation, in general thermal radiation, increases very rapidly with the temperature, and it has been shown by Lewis that his assumption leads quantitatively to an equation which agrees with the equation that Arrhenius obtained for the change in reaction velocity with the temperature.

"The assumption that every simple chemical reaction is accompanied by the absorption of light of one frequency and the emission of light of another frequency enabled Perrin to give a beautiful explanation of the phenomena of photo- and thermo-luminescence. Nevertheless in spite of the great value of this work in pointing out the influence of radiation in chemical phenomena, we cannot adopt the main contention that reactions are due solely to the influence of light and not at all to the molecular bombardment due to thermal motion.

"This is perhaps sufficiently shown by a consideration of those simple phenomena which we may regard as the prototypes of all chemical processes, namely, the resonance and ionization of gases. These phenomena are known to be caused either by radiation or by moving electrons, or by alpha particles, and they presumably can be caused by any other kind of molecular bombardment." p. 157.

"The older theory furnished an extremely happy explanation of the origin of color and its relation to the chemical properties of substances, as I attempted to show in my paper on the "Atom and the Molecule." According to that view, an electron in a position of constraint possesses, like any other elastic system, a natural period of vibration—this frequency being proportional to the magnitude of the constraint. Light which has this same period of vibration is capable of imparting energy to the electron resonator, and thus the electron absorbs light in that part of the spectrum which corresponds to its own natural frequency. In the majority of substances the electrons are held so tightly that their natural frequency falls in the ultraviolet region, and these are therefore capable of absorbing visible light. In other words, they are colorless. But under conditions which loosen the constraints within the molecule the frequency of the electrons is lowered until it corresponds to a visible frequency. The substance thus absorbing some part of the visible spectrum, and letting through other parts, is said to be colored.

"Since those changes in the condition of a molecule, such as the substitution of one radical for another, which are known from chemical evidence to loosen the structure of the molecule, and to render it more unsaturated and more active, prove to be the same kind of changes that convert a colorless into a colored substance, or which convert a substance with absorption in the violet into a substance with absorption in the red, this explanation of color seemed to be eminently satisfactory. Nevertheless the idea of a vibrating electron seems to be one which is not only alien to, but essentially incompatible with, the spirit of quantum theory.

"Fortunately the new theory of the discontinuity of chemical states furnishes a very similar and equally satisfactory explanation of color. When a molecule is in a state such that it may be changed to another state by a quantity of energy which, when divided by the Planck constant *h*, gives a number corresponding to the frequency of visible light, the substance is colored. Any process by which a colorless substance is converted into a colored substance may be regarded as one in which the molecule may be changed from one energy state to another state of only slightly different energy. In other words, with a new interpretation of our terms, we may still say that a colorless substance is converted into a colored substance by a loosening of the electronic structure," p. 160.

"Since we have been obliged here and there to take cognizance of the entering wedge of scientific bolshevism, which we call quantum theory, or the theory of discontinuity in nature, I cannot refrain from attempting to forecast some of the logical consequences which must follow from the new facts that have been discovered and the interpretation which they have been given. Such a forecast must of necessity be of the crudest sort, and can hardly do more than indicate the magnitude of the revolution in scientific thought which probably must occur before physical science can once more be a homogeneous whole, free from the most glaring inconsistencies and contradictions. . . .

"The recognition that electric and magnetic fields are essentially discontinuous leads us to suspect that there is no such thing as a continuous field of force; that a gradual acceleration accompanied by a gradual increase in kinetic energy is something which does not exist in nature. Rather we should consider that every system passes by steps, which may be small but are nevertheless finite, from one energy state to another.

"Finally we might even suspect that space and time could better be treated as discontinuous than as continuous, and represented by a counting method rather than by the methods of a continuous geometry. We might still call such a mathematical representation of space a geometry, but it would be of a very different sort from any existing geometry,—whether Euclidean or non-Euclidean, metrical or non-metrical. Its elements would be nothing but points and groups of points, and a distance would always be an integral number. With relation to some one point, other points would be classified according to whether they were separated from it by one step or two steps or *n* steps; and we might have a certain number of points in the class removed by one step, another number in the class removed by two steps, and so on.

"I hoped at one time to be able to find such a network geometry which, when the mesh was made exceedingly fine, would approximate to the properties of Euclidean geometry, but I am now convinced that such an attempt is hopeless. On the other hand, if we should consider a single atom, we might be able to state that this atom by itself determines a space which has just such properties of a network, which we might represent by 1 central point, 4 points of the class once removed, 9 points twice removed, 16 points in the third group, and 25 in the fourth. If now we should admit a pair of electrons at each of these points we should have (ignoring the sub-groups of Bohr) a representation of the shells about an atom containing respectively 2, 8, 18, 32 and 50, electrons. We should also find (once more ignoring the sub-groups) that in such a geometry the distance between two successive points would be quite without meaning, if we could consider but one atomic system.

"If, in some such way as I have crudely described, we could define the space of a single atom, then general space might be regarded as the composite of all the spaces of all the atoms, and in this space we could employ the ideas of extension, of distance, and the like, which are used in Euclidean geometry; with the same sort of approximate validity that we apply the principles of hydrodynamics to a system containing a large number of molecules, or the principles of electromagnetics to a field generated by many elementary charges," p. 163.

Wilder D. Bancroft

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. *Vol. IV. By J. W. Mellor. 25×18 cm; pp. x+ 1074. New York and London: Longmans, Green and Co., 1923. Price: $20.00.* The forth volume of this remarkable work is now out, and deals with the radium and actinium families and with beryllium, magnesium, zinc, cadmium, and mercury. As a preliminary to chapters on radium and radioactivity and on the architecture of the atom, there is a chapter on the structure of matter. On p. 2 we read that "the atom of an element can be defined as a substance whose parts are held together by a force superior to any which has yet been brought to bear upon it." On p. 4 the question is raised why closely related elements are so often associated in nature. "Chemists have long been struck with the peculiar way certain elements occur in the half-mile crust of the earth. Although no disturbing agent has been recognized at work in nature whereby the different kinds of elements are sorted like to like, yet certain groups of elements nearly always occur in juxtaposition. These individual elements are not plentifully distributed, and they are not easy to separate from one another—*pares cum paribus facillime congregantur*. For example, cobalt is perhaps never quite free from nickel, and *vice versa*; silver is almost invariably associated with lead ores and with gold; cadmium with zinc ores; selenium with the sulphur of pyrites; the members of the two groups of the platinum elements; the rare earths; etc. These associations and co-mixings cannot be entirely due to chance, for these elements are neither plentifully distributed nor have they any marked chemical affinity for one another. Consequently, it has been suggested that the elements in question were formed from some common material under almost identical conditions, and where slight variations in the conditions led to the almost simultaneous formation of closely related elements. Environment has determined the path of the evolution of the elements."

In 1849 "Foucault suggested the hypothesis that the incandescent gases in the arc light have the power of absorbing the yellow from sunlight as well as of emitting yellow light. The increase in the darkness of these lines (when a ray of sunlight is directed by means of lenses on to the glowing gases between the poles of an arc light which alone gave a spectrum with two yellow lines very prominent) is due to the absorbing power being greater than the emissive power. Foucault focussed the light from an incandescent carbon—which by itself gives a continuous spectrum—on to the incandescent gases between the carbon poles. Instead of getting the continuous spectrum of the incandescent carbon with yellow lines enhanced by the spectrum of the gases between the carbon poles, Foucault obtained a spectrum with the dark lines in the yellow portion. This experiment supported his hypothesis that the same kind of light, which a gas gives out when heated, will be arrested if the attempt be made to pass the light through the gas. Had Foucault known that the yellow lines were due to sodium, he would have recognized the origin of the Fraunhofer lines. This interpretation was made by Stokes, 1852. In 1859, Kirchhoff definitely settled the question," p. 5.

"Although the spectrum of each element is characteristic of that element and of no other, yet the spectrum of each of the five alkali metals can be resolved into four homologous series, such that every line in one spectrum is represented by a corresponding line in all the other spectra; and generally the spectra of related elements form natural or homologous groups. The corresponding lines do not necessarily all occur in the visible spectra, *e.g.* the dark red line of the rubidium spectrum corresponds with a line in the ultra-red in the other spectra; and the yellow lines of the sodium spectrum are homologous with lines in the ultra-violet spectra of the other elements. The spectra of related elements seem to be subject to a law of homology which is closely connected with their atomic weight. Each series of homologous lines appears to contract in passing from one element to another so that, as the atomic weight increases, the lines at the red end of the spectrum appear to open further apart, and at the violet end to draw closer together," p. 13.

"In the hotter stars little more than hydrogen can be detected, then follow hot stars with calcium, magnesium, and a few other elements super-added; then come cooler stars with more complex spectra corresponding with a greater variety of elements. The planets, of which our own is a type, are among the cooler ones. If the different suns and stars be arranged in a series, the order of the appearance of the elements in the cooling stars is approximately the order of their increasing complexity as deduced from the magnitude of their atomic weights," p. 20.

Under electric discharges in attenuated gases, p. 25, we read that "the negative glow with hydrogen is bluish white and it shows two spectra and Balmer's series; with nitrogen the colour is violet blue, and it shows band and line spectra; with helium the colour is green and with argon blue, while both show line spectra; with neon the colour is red; with oxygen the colour is greyish or yellowish-white, and there is a band spectrum; with carbon monoxide the colour is greyish-white, and there is a band spectrum; with carbon dioxide the colour is sky-blue; with chlorine the colour is green, yellowish-green with bromine, and oragne-yellow with iodine, bromine and iodine give a band spectrum. With sodium the color is yellow and it gives the D-line; with potassium the colour is pale blue, with rubidium blue, and with caesium greenish or greyish-white, and all give line spectra; with the vapours of cadmium and zinc the glow is red and there are line spectra; and with mercury vapour the colour is green or white and it gives a line spectrum."

On p. 43 under the photo-electric effect there is an interesting quotation from Millikan. "The physical theory, of which Einstein's equation was designed to be the symbolic expression, is so untenable that Einstein himself no longer holds to it, and we are in the position of having built a very perfect structure, and then knocked out entirely the underpinning without causing the building to fall. It stands complete and apparently well tested, but without any visible means of support. These supports must obviously exist, and the most fascinating problem of modern physics is to find them. . . . The atomic and electronic worlds have revealed themselves with definiteness and wonderful distinctness, but their relation to the world of aether waves is still a profound mystery."

Under positive rays, p. 51, we read that "the photographic plate registers the rays within a millionth of a second after their formation, so that if a chemical reaction were taking place in the tube, it is possible that the method would disclose the existence of transient intermediate compounds as well as the final products of the reaction. For example, with methane, CH_4, five lines occur corresponding with particles having the composition, C, CH, CH_2, CH_3, and CH_4. Phosgene, $COCl_2$, furnishes lines corresponding with particles having masses 99, 28, and 35.5, hence the decomposition proceeds by a separation of chlorine atoms from carbon monoxide without rupture of the carbon and oxygen atoms. No signs of a molecule NO_3 were observed during the oxidation of nitric oxide, NO, by oxygen."

"It is easy to understand how the belief that the base metals could be converted into gold dominated ancient and mediaeval chemistry. Facts were cited in its favour. The production of beads of silver and gold by the cupellation of metallic lead, and the reduction of metallic ores furnished direct evidence of the metamorphosis of the metals. Again, iron utensils in copper mines became coated with red copper when left in contact with the "mine water", so that the iron was seemingly transmuted into copper; similarly, the formation of white and yellow alloys by mixing copper and certain earths, seemed with the then imperfect knowledge, ample proof of transmutation. The dogma of transmutation thus appeared eminently plausible; it ran counter to no known laws of nature; it rested upon no extravagant assumptions; and it was sanctioned by the highest authorities. The immense labour which must have been expended in the fruitless pursuit of this chemical chimera by the alchemists is appalling. The quest was virtually abandoned with the advent of Lavoisier's balance," p. 148.

"The facts previously indicated show that not far from 2,000,000,000 cals. of heat are evolved during the degradation of one gram of radium. This is a quarter of a million times greater than is evolved by the combustion of a similar weight of coal. Hence it is inferred, from the atomic disintegration hypothesis of radioactivity, that the atoms of the radioactive elements, and probably also of other elements, have tremendous stores of potential energy, far greater than is developed during ordinary chemical reactions. The rate of degradation of the energy of the radioactive elements is comparatively slow, and is not available for doing useful work. The rate of evolution cannot be influenced by any known conditions and consequently the transmutation of the elements involves the discovery of methods of controlling these tremendous supplies of energy. Just as the application of a large quantity of electrical energy concentrated at the ends of a pair of platinum wires enabled Davy to decompose the alkali metals, so Ostwald, Ramsay, and others infer: *if ever one stable element is transmuted into another element, a large quantity of energy in a highly concentrated condition will be required.* This is quite in harmony with the alleged dissociation of the elements in the hotter stars (*q.v.*), where but a few elements are present, and where the temperature has been estimated at 25,000°. The 3000°-4000° obtained in some electrical furnaces appear but puny in comparison with the tremendous natural powers present in the hotter stars. There is some evidence that the swifter α-rays can furnish the necessary energy for atomic disruption.

"It has been pointed out that the formation of, say, gold from a metal atomically lighter, say tin, would require the expenditure of so much energy that even if the transformation were accomplished, it could not be a successful commercial process for the production of gold. On the other hand, the formation of gold from an atomically heavier metal, say lead, would liberate such an enormous amount of energy that the gold would be but an insignificant by-product, for the energy liberated during the process would have an enormously greater value than the metal. A. Schack discussed the thermo-dynamics of atomic energy," p. 150.

"From the early writings it is evident that at least three minerals of a totally different nature were called magnesia—(1) *magnesius lapis*, which is now represented by magnetite, was magnetic; (2) *magnesia nigra*, which is now represented by pyrolusite; and (3) a silver-white mineral, which could be conveniently fashioned in a lathe, or easily shaped and carved with hand tools, and which is probably now represented by steatite," p. 249.

"According to Willstätter, magnesium is an integral part of chlorophyll; and Kacher considered it to be an indispensable constituent of plants, saccharomyces, etc; the ashes of plants usually contain more calcium than magnesium, although the reverse is true for seeds. It is not known how the magnesium is distributed in the organs of plants, but it occurs in the cambium sap of pines as oxalate. Kayser found that the amount of magnesium in wine is proportional to the phosphoric acid, and that the smallest amount—0.001 percent MgO—was found in Pfälzer wine, and the greatest amount—0.040 percent MgO—in Malaga wine. Magnesium compounds occur in the skeleton, blood, and milk of animals. F. W. Clarke and W. C. Wheeler found it very exceptional for the inorganic parts of sea-organisms to be non-magnesian," p. 252.

"Magnesium is used for making illuminating powders for flash-light photography; and for star-shells for illumination in warfare; it is used as a deoxidizer in making bronzes, nickel-silver, and other alloys, it is used in conjunction with aluminum for making light alloys—*e.g.* magnalium; and it is used in dehydrating oils—*e.g.* aniline oil—etc. The compounds of magnesium are used medicinally; in making cements; and magnesia is employed for making the so-called magnesite bricks for lining basic steel furnaces, and electric steel furnaces," p. 265.

"H. T. Barnes and G. W. Scherer showed that with magnesium and aluminum electrodes in contact with water containing dissolved air the electromotive force rises slowly to about one volt, although the metals are close together in the electrochemical series; this is due to the formation of hydrogen peroxide by the action on aluminum of water containing dissolved air. When free hydrogen peroxide is added to the aluminum compartment, the electromotive forces rises to about two volts and then falls gradually as the hydrogen peroxide is decomposed," p. 267.

Although dolomite occurs in cubic miles in the Dolomite Alps, the chemist has never succeeded in making dolomite under conditions at all comparable to those which occur in nature, p. 372. This is a very interesting problem and it is quite possible, as Mellor suggests, that we have not taken the pressure factor sufficiently into account.

"The term brass is mentioned several times by the biblical writers—nearly 4000 years B.C., for instance, we are told in Genesis, that Tubalcain was a worker in brass and iron; and the brass or bronze looking glasses of women are mentioned in Exodus. There are also frequent references to brass or bronze in the early writings of Homer, about 1000 B.C., and of Hesiod, about 700 B.C. So far as we can gather, the early writers confused copper, brass, and bronze because the same term was employed for any or all these metals. The word rendered brass should be translated bronze. It is known that it was customary in very early times for women to wear a bronze mirror as an article of dress; Klaproth has analyzed one such, and found: copper, 62; tin, 32; and lead, 6 per cent. . . .

"It is probable that the alloy known as orichalcum or brass, tombac, pinchbeck, etc., was first discovered by smelting cupriferous zinc ores which yielded not copper but brass. Mines that contained ores, from which the gold-coloured metal was produced, were held in the highest esteem, and the early brasses seem to have been obtained by the smelting of such ores from mines in Laurium (near Athens), Sardinia, and Cyprus. In course of time, it was observed, possibly by accident, that an earth, which was probably calamine, when added to molten copper gave it a yellow colour; and this as a method of preparation was found to be more convenient than procuring the brass from zinciferous copper ores. This is the method to which the pseudo-Aristotle above refers. According to E. von Bibra, the Greeks were not acquainted with the manufacture of brass, but that alloy was made about the time of Augustus, near the beginning of the Christian era, by heating copper with certain earths—presumably containing zinc, *e.g.* calamine, galmei, or tutty—mixed with carbon. Brass was thus known to the Romans; and about the eleventh century, the process of manufacture was described by the monk Theophilus. As the zinc was reduced, it alloyed with the copper by cementation, forming the golden-yellow colour characteristic of a low-zinc brass. It is remarkable that the same word *cadmia* should have been employed for both the zinciferous ore and the flue-dust—an impure zinc oxide—found in furnaces smelting zinciferous ores. According to J. Beckmann, the term *tutia*, employed by Avicenna in the eleventh century, seems to have been used in a similar manner. A work attributed to Zosimus of Panopolis stated that brass is made by melting Cyprian copper with *tutia*. In spite of this, the furnace-calamine, which collected about the furnaces at Rammelsberg, was rejected as useless until the middle of the sixteenth century, when E. Ebener, about 1548, discovered that it could be employed in making brass. . . .

"According to Cicero, who wrote near the beginning of our era, Roman coins made from orichalcum were indistinguishable from gold, and he raised the ethical question whether an honest man should acquaint a person who was really selling *aurum* but thought he was selling *orichalcum*, or should he buy for a penny what was worth a thousand times as much? The only metal which the Romans could have so mistaken for gold is the alloy of copper and zinc now called brass", p. 398. Since bargaining in the days of the Romans was carried on under the motto "*Caveat emptor,*" Cicero's question indicated a distinct ethical advance.

"If the vapor of zinc be too much diluted with other gases, it can condense only to zinc fume and not into fluid metal. The greater the proportion of these gases the greater the proportion of zinc fume. This fact, and the back reaction, indicated above, explains why all attempts to reduce the oxide in reverberatory and blast furnaces have not been satisfactory. Either zinc oxide or the troublesome zinc fume is obtained," p. 413. The reviewer doubts the volume of gas having any effect on the production of zinc fume unless there is oxidation.

"Zinc oxide mixed with oil dries to a hard film, basic lead carbonate or white lead dries to a much softer and more chalk-like surface, just as zinc added to certain metals gives hardness to the resulting alloy, so, by analogy, zinc oxide added to white lead produces a pigment which when mixed with oil and applied as a paint gives a harder and more durable surface than the white lead alone," p. 518. This analogy seems painfully superficial to the reviewer. A plain statement of the facts is better than an explanation which is not so.

"The crystals of cadmium sulphide are yellow when in tufts of hairlike needles, but larger crystals are brownish-yellow. The different colours of amorphous cadmium sulphide are due to the relative amounts of light transmitted and reflected, since the colour of a substance by reflected light depends on the character and relative amounts of light reflected directly from the external surfaces, and indirectly from internal surfaces—*i.e.* after having passed into the substance and been reflected out. Greenockite absorbs the blue and violet and part of the green spectral rays, the remainder are freely transmitted; a comparatively large amount of blue light is directly reflected by the plane bright faces of the crystals about 1 mm. in diameter, and a small amount of red, orange, yellow, and green is reflected after passing through the surface layer. The combined effect of all the reflected light is a lustrous dark yellow to yellowish green or dark citron-yellow. Crystals 0.01 mm. in diameter reflect about the same amount of blue light directly, and much more of that which has penetrated the surface so that the resulting colour is a brilliant yellow. Massed crystals with a dull surface have a light yellowish-brown or citron colour. The grains of powered crystals usually have bright but not plane surfaces and give a brilliant orange powder, for there is less direct reflection, and more indirect reflection of light from the interior which has lost more green and yellow than with a powder having plane-faced fragments. The colour of the amorphous sulphide is explained in a similar manner. The amorphous sulphide absorbs more strongly in the yellow and green and, by transmitted light, its colour is orange yellow in films 0.01 mm. thick, and yellow in films 0.001 mm. thick. The powdered amorphous sulphide with grains 0.0001 to 0.001 mm. in diameter is bright yellow with a tinge of orange, and with grains 0.004 to 0.007 mm. in diameter, or compact aggregates of smaller globules, is bright orange," p. 593.

"Mercury is not mentioned by Moses in the Pentateuch, nor by the earlier Greek writers, and Kopp, therefore inferred that the discovery of this element came later than that of gold, silver, copper, tin, lead or, iron. Berthelot believed that tin amalgam and copper amalgam were known to the ancient Egyptians under the name *asem*. According to Seligmann, the discovery by Schliemann of a small vessel full of mercury in a grave at Kurna, and estimated to belong to the sixteenth or fifteenth century B.C., shows that this element must have been known a very long time. Weiskopf was of the opinion that this element was probably known to the Phoenicians and Carthaginians 700 B.C. . . . . Discoveries of stone hammers, arrow-heads, wooden plates, and coins, made around Monte Amiata, Italy, show that these mines were worked for cinnabar by the Etruscans, and later by the Greeks and Romans," p. 695.

Under physical properties of mercuric oxide, there is a case of apparent catalysis, p. 779, which should be studied more carefully. "Mercuric oxide forms complexes with many organic compounds. According to Auld and Hantzsch, freshly precipitated mercuric oxide does not dissolve in acetone, but it dissolves readily if a trace of alkali hydroxide is present; it behaves similarly with acetaldehyde; and it does not dissolve in acetophenone unless the mixture is heated to 100°" The following statement, p. 826, should also be investigated. "Zenghelis found that hydrogen under ordinary conditions does not reduce a solution of mercuric chloride, but it does so if the gas is allowed to bubble into the solution through a filter-paper extraction thimble."

The reviewer notes with sorrow that the author uses the formula HgCl when discussing mercurous chloride electrodes, p. 738. Since the mercurous ion has been proved to be $Hg_2^{\cdot\cdot}$, the formula for mercurous chloride should be written Hg_2Cl_2 in all electrochemical processes regardless of what the formula of the vapor may be.

Wilder D. Bancroft

Elektrochemie nichtwässriger Lösungen. *By Paul Walden. 24×17 cm; pp. xi+516. Leipzig: Johann Barth, 1924.* In the preface the author says, p. vii, that he is well aware that an "Electrochemistry of Non-aqueous Solutions" requires a different treatment from an "Electrochemistry of Aqueous Solutions." "The scientific foundation—the electrolytic dissociation theory of Arrhenius and the osmotic solution theory of van't Hoff—is common to both electrochemistries. The electrochemistry of aqueous solutions has deeper roots and may be considered at present as generally accepted and as having proved its value technically as well as scientifically. The electrochemistry of non-aqueous solutions has gone in more for breadth than depth. The number and variety of the non-aqueous solvents causes questions and relations to come up which are either unknown or of minor importance in aqueous solutions. In spite of the great amount of experimental work which has been done, many problems still require confirmation as well as solution. Consequently ripe and unripe fruit must be piled together in this book. The field of non-aqueous solutions shows in general a large swarm of anomalies, which are often enough considered as contradictions to the two, previously mentioned, classical theories. In order to keep these difficulties, anomalies, and contradictions to a minimum, increased attention must be paid to the solute on the one hand and to the individual solvents on the other hand. In addition to the chemical nature, it is chiefly the dielectric constant, which, like a red cord, guides us in our task of understanding and describing qualitatively, and to some extent quantitatively, all the peculiarities of the solvent. In the case of the solute the numerous anomalies can be referred to the formation of polymers, autocomplexes, solvates, and complex ions."

The subject is presented under the general sub-heads: historical development; conductance of solvents; conductance of solutions; effect of temperature and viscosity on conductance; transference numbers and migration velocities; electrolytic dissociation; potential differences; relation between electrolytic dissociation and dielectric constant; chemical reactions of electrolytes in non-aqueous solutions; solubility of electrolytes in non-aqueous solutions.

The reviewer was delighted to see that Walden appreciates the value of Kahlenberg's work, pp. 19, 391. "Both Traube and Kahlenberg have helped along the electrolytic dissociation theory by their criticism of it. The deliberate emphasis on the over-hasty generalizations (for instance, that all reactions are ion reactions), the logical criticism of the insufficiently explained causes for the dissociation into ions and the contradictions in the enormous field of non-aqueous solutions which often rested on inaccurate observations, the planning and carrying out of his own clever experiments on instantaneous reactions in non-conducting solutions, all these can be considered as positive achievements by Kahlenberg because they made it necessary for the upholders of the dissociation theory to make new experiments to clear up their views, to make limitations, and to reconsider their auxiliary assumptions . . . . Quite irrespective of the question whether Kahlenberg succeeded in accumulating enough dynamite to destroy the osmotic and electrolytic solution theories, this experimental work is full of interest, because it calls attention to a neglected field, which one can consider as a border-land between organic chemistry and physical chemistry."

There are interesting paragraphs on hydration, p. 33; on the relation of the dielectric constant to other properties, p. 42; on the ionization of binary salts, p. 89; on the calculation of the molecular conductance at infinite dilution, p. 96; on the hypothesis of complete dissociation, p. 108; on the dilution law, p. 146; on the diameters of the ions in non-aqueous solutions, p. 191; on abnormal ions, p. 195; on the conductance of aluminum bromide dissolved in bromine, p. 211; on the causes of anomalous conductances, p. 236; on the colors of the ions, p. 287; on the electrocapillary curves in non-aqueous solvents, p. 314; on decomposition voltages in pyridine, p. 322; on hydrogen as a halogen, p. 331; on the corrosion of zinc by hydrochloric acid dissolved in ether, p. 384; on conduction in gases during chemical reactions, p. 398; and on the relation between solubility and the dielectric constant, p. 430.

The following summary is given of electrolysis in non-aqueous solvents, p. 332:—"The behavior of electrolytes in non-aqueous solvents, so far as electrolysis is concerned, is the same in the fundamentals as in aqueous solutions. Firstly, electrolysis occurs even in so-called insulators such as benzene. Secondly, the products set free at the electrodes correspond to the known elements and compounds obtained by electrolysis in aqueous solutions; but the chemical action between discharged ions and solvent can be modified so easily by a suitable choice of solvent that one can get products which are impossible in aqueous solutions (consider solutions in pyridine, acetone, nitrobenzene, ether, chloroform, ethyl bromide, benzene; aluminum bromide, ammonia, sulphur dioxide, bromine, iodine monochloride, iodine monobromide, iodine trichloride, the halide acids). Thirdly, Faraday's law holds absolutely for the field of non-aqueous solutions."

Under reactions in inorganic solvents, we find the following summary p., 397:—

I. Chemical reactions between inorganic electrolytes, which are typical, rapid ion reactions in aqueous solutions, take place also in non-aqueous, organic and inorganic solvents.

1. These reactions occur in media, in which a more or less perceptible formation of ions occur, as, for instance, in the alcohols and nitriles, or in liquid ammonia and sulphur dioxide. In consequence of the low dissociating powers of the media, the dissolved electrolytes are often polymerized; dissociation occurs in stages, intermediate ions (complex ions) are formed which may be partially solvated and which take part in the reactions along with the normal ions (as determined in aqueous solutions).

2. In so-called insulators such as hydrocarbons and their halogen substitution products or in media with very low dielectric constants (less than 2.2), such reactions occur, especially precipitation reactions. The solubility relations of the newly-formed products are the determining feature, and reactions which give rise to insoluble substances run nearly quantitatively to an end. More careful investigations in these cases show the existence of ions, for instance in benzene, ether, and chloroform solutions.

II. In addition to the known ion reactions the non-aqueous solutions give us instances of new, rapidly occurring, reactions between substances which do not belong to the recognized salt type or which are not considered as electrolytes (for instance, the reactions with halogen aryls, metal aryls, etc). The electrolytic nature of these substances has been proved conclusively and therefore the action of ions may be postulated.

One would suppose that the size of the book would have made it impossible to include the more recent work; but there is a reference, p. 323, to the paper by Conant and Lutz on a quinhydrone electrode in acetone. About the only fundamental error which the reviewer was competent to detect is on p. 60, where the author postulates that fluorine is set free in the electrolysis of aqueous hydrofluoric acid but reacts at once with water, regenerating hydrofluoric acid. Of course, this does not happen at all. That matter should have been cleared up once for all by LeBlanc's experiments on the decomposition voltages of the bases over thirty years ago.

The author has done a monumental piece of work in compiling this book and we hope that the book will be a help and an inspiration to many for years to come.

Wilder D. Bancroft

Physikalische Chemie. *By Alfred Benrath. Vol VIII. 22×15 cm; pp. viii + 107. Dresden and Leipzig, 1923. Price: fifty cents.* This is another of the series edited by Liesegang which aims to post people on the work done during the war. This volume summarizes the work published between 1914 and 1922. In the preface the author says: "There are two points of view from which a progress report can be written. One can arrange the extracts chronologically or one can follow the development of certain lines of thought. The latter has been adopted because it is the more interesting. It cannot be denied, however, that the report is less complete in consequence because no place can be found for many papers which are really the dying echoes of interests which have passed. On the other hand the beginnings of a new development often lie back of the interval on which one is reporting and one must therefore go back quite a way. Consequently the report acquires something of the character of a text-book but differs from it in not adopting a dogmatic treatment. The circle of readers is also determined by adopting this form of report. It does not consist of those directly interested because they already know the developments. It must consist of the chemists who are active in other branches but who wish to keep posted on the general advances in the science. They will receive an unexpected stimulus and will be surprised to learn that the apparently very sound theoretical foundations, on which physical chemistry rests, can scarcely carry the structure. The old pillars are shored up and replaced here and there by new ones. The highly developed experimental technique is continually turning out such a mass of new facts that the man with the systematic mind doubts the possibility of classifying everything under the existing theory. . . . We must hope that some day a new genius will appear who will remodel the collapsing science by the power of his ideas."

The subject is divided into two parts: chemically pure substances and solutions, twenty-two pages being devoted to the first and seventy-six to the second. There is a very good summary of the changes of properties of pure substances with the temperature. Under allotropy, p. 14, the author adopts the theory of Smits without modification and considers that all metals consist of an indefinite solid solution of two or more modifications. It does not trouble the author that the work of Cohen, which he cites, lends no support to this view although furnishing much data to show the prevalence of allotropic modifications among metals. He also considers that Smits has solved the question of passive iron and that passive iron is fundamentally different from passive lead in the form of lead peroxide. On p. 33 he draws the conclusion that all liquids are associated, apparently because it is not proved that they are not. He quotes approvingly, p. 35, the assumption (which he calls a law) of Dolezalek that the properties of a solution are always additive if one assumes the right molecular weights. He wishes to account for the peculiarities of concentrated and non-aqueous solutions by postulating that the activities of the ions increase with the concentration and decrease with increasing viscosity. He accepts, pp. 57, 74, Bjerrum's theory of complete dissociation but draws the line, p. 95, at determining the degree of hydration of the ions from the application of Stokes' law to the movement of the ions under electrical stress.

This book is not critical in any proper sense of the term and one cannot congratulate the editor on his choice of an author.

Wilder D. Bancroft

Einführung in die Kolloidchemie, *By Victor Pöschl. Sixth improved edition. 23×16 cm; pp. xii+158. Dresden and Leipzig: Theodor Steinkopff, 1923. Price: 70 cts.* The first edition appeared in 1908 and was probably a very good book. It has not changed with each edition as rapidly as the subject has, so that now the book does not represent the modern point of view. In the list of scientific journals, for instance, the Journal of Physical Chemistry does not appear.

The subject is presented under the general heads: historical development of colloid chemistry; characteristics of the colloidal state; properties of colloidal solutions and gels; methods for making colloidal solutions; views on the nature of the colloidal state; significance of colloid chemistry for other sciences; significance of colloid chemistry for cemchial industry.

In the chapter on the theories of the colloidal state the author considers the solution theory, the adsorption theory, and the suspension theory as more or less mutually exclusive. Practically nobody believes that colloidal silver, for instance, is in true solution and practically nobody believes that colloidal silver would stay in suspension if the particles were not kept from coalescing by adsorbed ions. Consequently it is an absolute waste of time to discuss the relative merits of an adsorption theory and a suspension theory. It is rather pitiful to think of a man being a pioneer at the time of a first edition and apparently a hopeless back number at the time of the latest edition.

Among the industrial products which are essentially colloidal, the author cites, p. 140: starch, cellulose, celluloid, glue, leather, resins, rubber, artificial silk, paper, photographic plates and papers, soap, etc. Among the sciences which are interested in colloid chemistry the author cites biology, physiology, pathology, pharmacology, agriculture, mineralogy, and meteorology.

Wilder D. Bancroft

Die Elektrochemie der wässerigen Losungen. *By Fritz Foerster. Fourth unrevised edition. 25×17 cm; pp. xx+900. Leipzig: Johann A. Barth, 1923.* The third edition was reviewed about two years ago (26, 493). The fourth edition is exactly like the third and corresponds to what we call another printing. There is therefore nothing to add to the previous review except the warning that this is not a new edition in any real sense of the word.

Wilder D. Bancroft

THE SIZE-FREQUENCY DISTRIBUTION OF GRAINS OF SILVER HALIDE IN PHOTOGRAPHIC EMULSIONS AND ITS RELATION TO SENSITOMETRIC CHARACTERISTICS[1]

VI. *Photographic Densities derived from Size-Frequency Data*[2]

96-9[illegible]

BY E. P. WIGHTMAN, A. P. H. TRIVELLI AND S. E. SHEPPARD

The object of the present work was to find a method of deriving experimentally the densities for any given exposures in the characteristic H. and D. (density-log exposure) curve of a simple photographic emulsion from its grain size-frequency distribution.

The Size-Frequency Determination

One-grain-layer plates of a Seed Lantern slide emulsion were prepared, on thin plate glass strips, 5 cm. × 12.5 cm. × about 1-2 mm. thick, in the manner previously described by us[3].

The size-frequency distribution measurements of these were made by the method also previously described[4]. In order to obtain a high degree of accuracy in the experimental size-frequency data more than 84000 grains were measured, 17,500 alone to determine the frequency curve of the unexposed grains. For the latter more than 100 photomicrographs were made from widely distributed fields over several plates.

It was found on plotting the data that neither the simple exponential equation

$$y = \mathrm{A}e^{-kx} \qquad (1)$$

nor the modified Gaussian type

$$y = \mathrm{A}e^{-k(x-\alpha)^2} \qquad (2)$$

would truly represent the observed distribution.

The Gaussian type (Equation 2) had been applied to all data displaying a maximum, but the tail of the applied curve was frequently too steep and short to fit the observed values. That this formula is fundamentally incorrect in such cases was demonstrated by Mr. Loveland of this Laboratory by plotting the logarithms of the observed frequencies against the class size. If the data are rigidly represented by the above formula (Equation 2), then the curve just plotted should have the form of an inverted parabola since by taking the logarithms of both sides equation (2) can be put in the form

$$(x-\alpha)^2 = -4a(y'-\beta) \qquad (3)$$

where $y' = \ln y$, $a = \frac{1}{4k}$, and $\beta = \ln \mathrm{A}$. This, however, was found not to be the case.

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[1] Communication No. 200 from the Research Laboratory of the Eastman Kodak Company.

[2] Presented in abstract before the Am. Chem. Soc., Milwaukee Meeting, September (1923).

[3] E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard: J. Phys. Chem. 27, 1 (1923).

[4] Ibid. loc. cit.

Mr. Loveland then tried plotting the logarithms of both the x and y values and found that the locus of the points can be well represented by the general inverted parabolic formula

$$(x' - \alpha)^2 = -4a(y' - \beta) \qquad (4)$$

If we let $x' = \ln x$ and $y' = \ln y$, and as above, $a = \frac{1}{4k}$ and $\beta = \ln A$, this expression can be converted into the form

$$y = Ae^{-k(\ln x - \alpha)^2} \qquad (5)$$

which is found to fit the observed size-frequency data for certain emulsions much more closely than equation (2) because of its higher maximum and longer tail. We will henceforth call this the "Loveland equation", although it was found later that it can be derived by a different method, namely that of Kapteyn and van Uven.

Size-Frequency Curves and their Physical Meaning

We have already pointed out[1] that equations (1) and (2) have a definite physical meaning, in that "the starting point in the determination of dispersity and distribution of grains formed in precipitation appears to be the preliminary distribution of ionic and molecular velocities in the reaction solution.

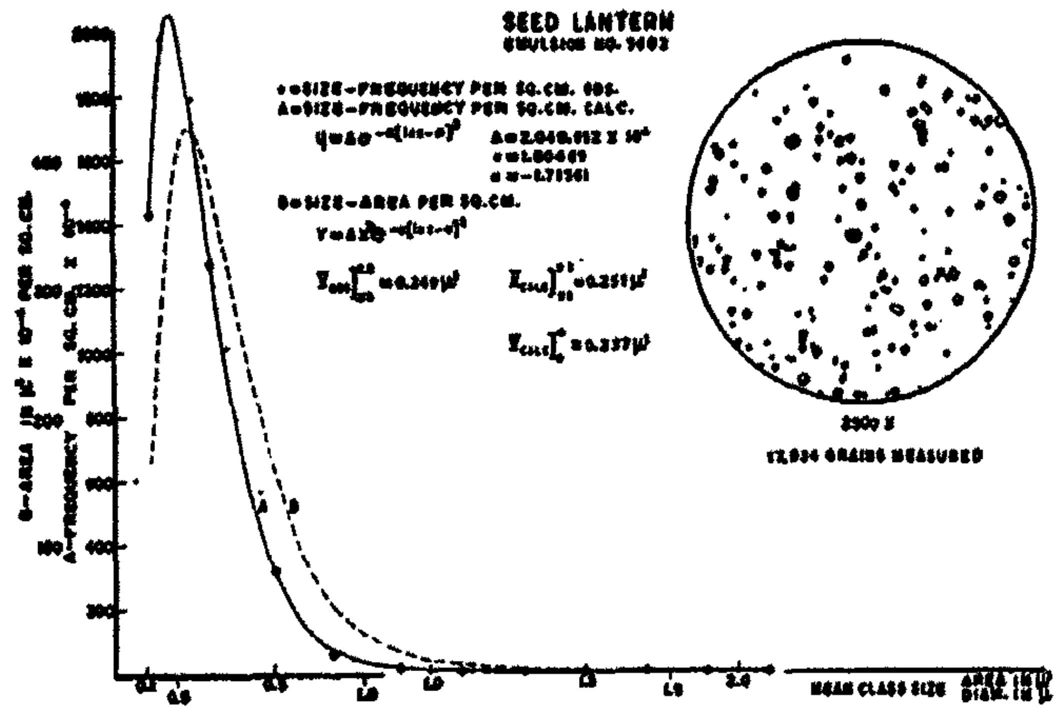

FIG. 1

"This will be represented by Maxwell's 'error function' in some form. Thus, the number of ions having velocities between the limits v and $v + dv$ will be

$$dn = CNe^{-3v^2/\bar{v}^2} \cdot v^2 dv$$

where N is the total number in the system, $\bar{v}$ is the root-mean-square velocity and C is a constant.

"Further, the velocities (Brownian movement) of the first colloidal particles of insoluble precipitate formed will be similarly distributed—both as regards translational and rotational movements".

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[1] E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard: Trans. Faraday Soc., 29, 270 (1923).

The effect of stirring and other factors is likewise considered, and it is pointed out that the actual emulsions, in many instances follow simple asymmetrical error functions which are similar to or can be derived directly from the Maxwellian distribution.

The physical meaning of the Loveland equation, however, is not quite apparent at first sight. Our attention has just been directed by Prof. Zernike, of Groningen, Holland, to a book by J. C. Kapteyn and M. van Uven[1], in which the physical significance of such an equation is discussed. The equation with the logarithm in the exponent results from the assumption that the growth of the grains is proportional to the size of the grains at any instant. This is a quite reasonable assumption to make and is probably true for a large number of cases.

We give in Table I a comparison of data calculated by equations (2) and (5) with the observed values. The data are plotted in Fig. 1.

TABLE I

Comparison of Observed and Calculated Values of Size-Frequency Seed Lantern Emulsion

Class Size in μ^2	y obs. $\times 10^{-4}$ per cm²	Equa. (5) y calc. $\times 10^{-4}$/cm²	y calc. $\times 10^{-4}$/cm²
0.065	600.27*		
0.115	1428.94	1428.79	1429.45
0.15	1976.30*		
0.18=A		2049.95	
0.20		2008.65	
0.25	1791.59*		
0.30	1276.97	1278.08	1275.44
0.35	1014.26*		
0.40		651.56	
0.45	562.31*		
0.50	317.97	310.66	325.62
0.70	58.90	73.15	23.79
0.90	16.63	19.02	0.50
1.10	5.52	5.58	0.003
1.30	1.69	1.76	0
1.50	1.42	0.61	0
1.70	0.88	0.23	0
1.90	0.18	0.09	0
2.10	0.18	0.04	0

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*These values were determined separately on a smaller number of grains than those originally measured, in order to see if the experimental values indicated a maximum, and if this were at all comparable with that obtained by equation (5).

[1] J. C. Kapteyn and M. Van Uven: Skew Frequency Curves in Biology and Statistics, 2nd Paper, Astronomical Laboratory, Groningen, Holland (1916).

We can now get a clearer picture of how an emulsion of simple type is formed:

The molecules in the reacting solutions are brought together and start forming very minute grains of different sizes, due to the variation in molecular velocities. By "size" in this case we mean "surface", although practically we use "projective area", which may be considered as approximately proportional to total surface where the grains are for the most part tabular as in some emulsions, or mostly nearly spherical as in other emulsions. Now, once the grains have started forming in different sizes they continue to grow, each proportionally to its own size at any moment, until an equilibrium condition is reached. In the so-called ripening process this same condition would tend to hold.

We can imagine, however, that there may be certain factors which will make the growth either independent of the preexistent sizes on the one hand, or may modify the strict proportionality on the other.

We shall turn now to certain observations made in the third paper of this series.[1] It was noted there that equations of the same fundamental form appeared, at least approximately, to be applicable to both uniform diameter and uniform area classification, although mathematically this was inexplicable. In other words, equation (14) in that paper, i.e.,

$$y = y_0 e^{-k(z-\alpha)^2}$$

where z represents the diameter of the grain, cannot be converted mathematically into an equation of the same form by replacing z by its equivalent area, since the variable in the exponent is then changed to the one-half power.

On the other hand, it is seen from the following that equation (5) above, can be so converted:

Let $x =$ the projective area corresponding to the diameter z, then

$$x = \pi z^2$$

Substituting this in equation (5) we get

$$\begin{aligned} y &= \mathrm{A}e^{-k(\ln(\pi z^2)-\alpha)^2} \\ &= \mathrm{A}e^{-k(2\ln z + 2\ln\pi - \alpha)^2} \\ &= \mathrm{A}e^{-k'(\ln z-\alpha')^2} \end{aligned}$$

where $$k' = k/\sqrt{2}, \text{ and } \alpha' = \frac{\alpha - 2\ln\pi}{2}$$

Thus we have changed the constants but not the variable, and hence the fundamental form of the equation remains the same.

The Results of Photographic Exposure and Development

A series of one-grain-layer plates coated in the same way, and with the same emulsion as above stated, were exposed in a Jones non-intermittent sensitometer, to uniform intensity of light for a series of times increasing in

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[1] Wightman, Trivelli and Sheppard: J. Phys. Chem. 27, 1 (1923).

1/2 powers of 2. These plates were developed to approximately gamma-infinity, and the developed silver was removed by means of a CrO_3-H_2SO_4 solution (0.5% each).

The residual grains were then photomicrographed, as in the case of the unexposed plates, and the size-frequency distributions of the residual grains in each step were determined per unit area of the plate. The values from six plates were averaged (See Table II.) and the resulting values for the residual grains on each step were subtracted from the total unexposed grains (development fog being negligible), thus giving the size-frequencies of developable grains per unit area of plate. By dividing the resulting values by those for the original area-distribution we got the percentage developable grains in each class. These are given in Table III. together with the approximate exposures in ergs.

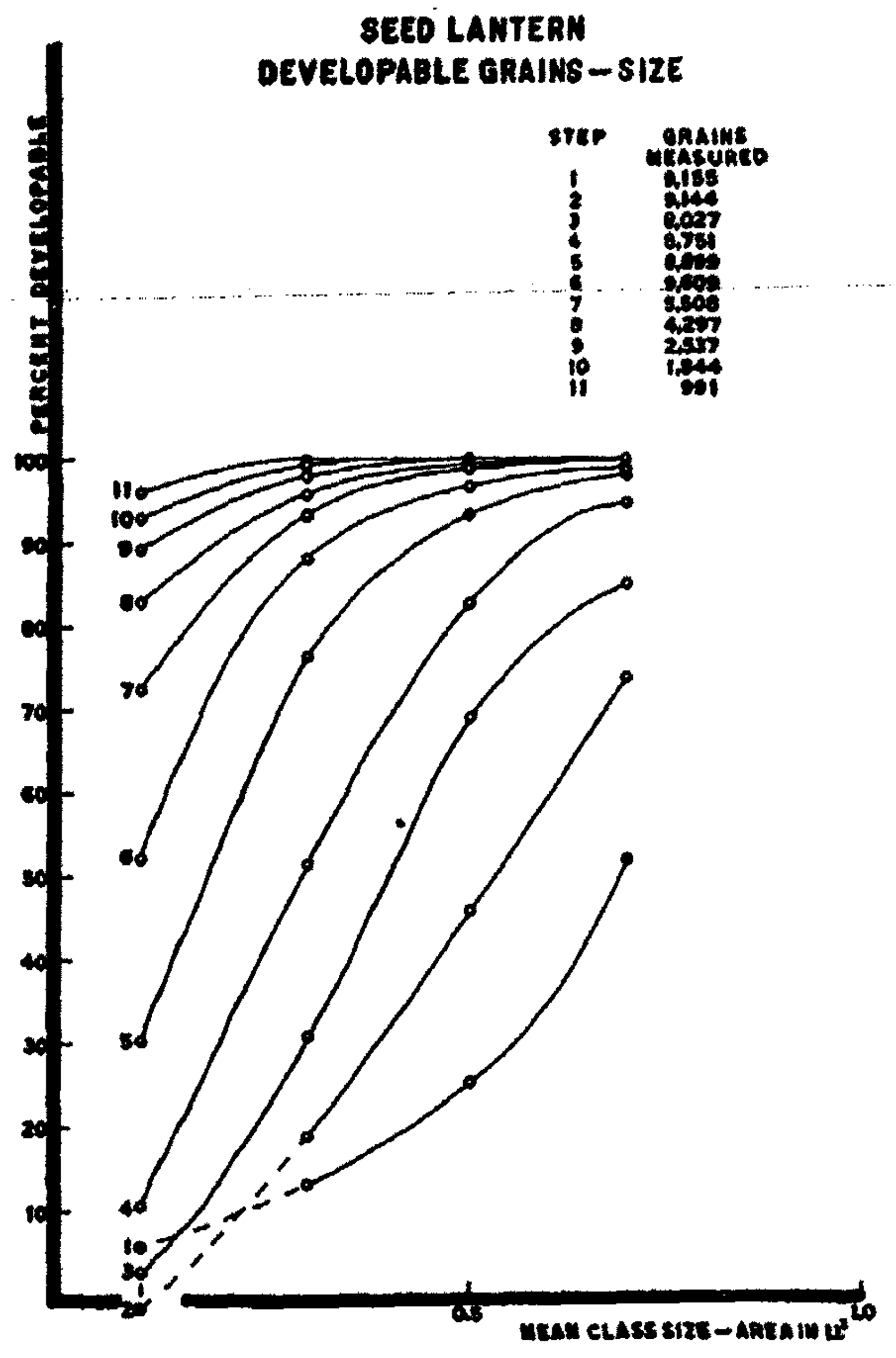

FIG. 2

It should be noted that these values for the percentage developable grains were obtained entirely from the experimental data without attempting to

TABLE II

Size-Frequency of Residual Grains per cm² of Plate × 10^{-4}

Step No.	Mean Class Size 0.115	0.3	0.5	0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.1	Exp. in ergs*
0	1428.9	1277.0	317.97	58.90	16.63	5.52	1.69	1.42	0.88	0.18	0.18	0
1	1347.5	1110.1	237.38	28.27	8.00	2.38	1.79	0.91				150
2	1452.2	1035.0	171.92	15.42	2.08	1.16	0.30	0.58				212
3	1392.4	882.12	98.39	8.81	1.19	0.30	0.59					300
4	1278.2	621.90	47.25	3.12	0.88	0.22						424
5	995.12	302.69	21.03	1.18	0.59							600
6	685.29	152.45	10.60	0.71	0.18							848
7	394.37	85.41	3.40									1200
8	245.02	54.34	1.45									1696
9	152.53	26.03	0.21									2400
10	100.13	8.23										3392
11	56.23	1.96										4800

---

*These exposures are only approximate, and cover only the visible region of the spectrum. The exposures were made at 1 m. from an opal glass, appature 320 cm², illuminated with a 250 W. concentrated filament tungsten lamp at 110 V. The shortest exposure was 4 sec. and the remaining exposures increased in 1/2 powers of 2. Total exposure on the first step was determined by means of a thermopile, and from the color-temperature curve of the lamp, the visible portion of this total curve was found by means of the Wien-Boltzmann law.

smooth them out. In spite of that, they show a remarkable smoothness as can be seen from Figs. 2 and 3, where the percentage developable grains are plotted against mean class size for the eleven exposure steps and four class-sizes. Values for other class-sizes were not plotted because of their comparatively great inaccuracy.

A complete discussion of the size-frequency curves of this emulsion and of the residual grains after exposure and development will be given in a later paper.

These values of percentage developable grains are being used by Dr. L. Silberstein for testing his theory of exposure by discrete light quanta, and they will also be used by us to test the theory which we had previously put forward[1] for obtaining the relation between the frequency distribution and the characteristic exposure-density curve.

It should also be said that an effort will be made to determine for comparison, the theoretical frequency curves and percentage developable grains on the basis of the quantum theory.

Derivation of Density from Size-Frequency Distribution

As we have shown previously[2], the size-frequency distribution in itself is of no great importance. We therefore obtained the theoretical (projective) area-distribution by means of the equation

$$y = xy = \mathrm{A}xe^{-\mathrm{k}(\ln x - \alpha)^2} \qquad (6)$$

The resulting curve is represented by the dotted line in Fig. 1. Practically, the area-distribution was obtained by multiplying the frequencies in each class-size by the mean class-size. This was done for each exposure step and the areas of residual grains were subtracted from the corresponding areas of the original unexposed emulsion. Table IV gives the projective areas of residual grains per class for the different exposure steps, and Table V the corresponding values for the developable grains. The data in Table V for 4 classes are plotted as dotted lines in Fig. 3, area of grains against log exposure.

Before the density of developed grains can be obtained, however, it is necessary to know the expansion ratio or increase in projective area of the grains of each class in being developed from silver bromide to silver. This was found by photomicrographing the same grains before and after development and taking the ratio of their sizes in the two cases.

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[1] Wightman Trivelli and Sheppard: J. Phys. Chem. 27, 141 (1923); J. Franklin Inst., 194, 485 (1922).

[2] Loc. cit.

TABLE III

Percentage Developable Grains with Varying Exposure

Step No.	Mean Class Size 0.115	0.3	0.5	0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.1	Exp. in ergs*
1	5.70	13.07	25.35	52.01	51.87	56.86		44.92	100	100	100	150
2		18.95	45.93	73.82	87.51	78.96	82.31	59.04	100	100	100	212
3	2.56	30.92	69.06	85.04	92.86	94.65	65.22	100	100	100	100	300
4	10.55	51.30	85.14	94.70	94.70	95.94	100	100	100	100	100	424
5	30.36	76.30	93.39	98.00	96.43	100	100	100*	100	100	100	600
6	52.04	88.06	96.67	98.80	98.94	100	100	100	100	100	100	848
7	72.40	93.31	98.93	100	100	100	100	100	100	100	100	1200
8	82.85	95.74	99.64	100	100	100	100	100	100	100	100	1696
9	89.33	97.96	99.34	100	100	100	100	100	100	100	100	2400
10	92.99	99.37	100	100	100	100	100	100	100	100	100	3392
11	96.07	99.85	100	100	100	100	100	100	100	100	100	4800

*See footnote Table II.

TABLE IV

Projective Area of Residual Grains per Class, in μ^2

Step No.	Mean Class Size 0.115	0.3	0.5	0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.1	Exp. in ergs
0	157.18	383.00	158.99	41.23	14.97	6.07	2.19	2.13	1.50	0.34	0.37	0
1	148.23	333.03	118.69	19.79	7.20	2.62	2.32	1.37				150
2	159.74	310.51	85.96	10.79	1.87	1.28	0.39	0.87				212
3	153.16	264.64	49.20	6.17	1.07	0.33	0.76					300
4	140.60	186.57	23.63	2.19	0.79	0.25						424
5	109.46	90.81	10.52	0.83	0.53							600
6	75.38	45.73	5.30	0.50	0.16							848
7	43.38	25.62	1.70									1200
8	26.95	16.30	0.73									1696
9	16.78	7.81	0.11									2400
10	11.02	2.47										3392
11	6.19	0.59										4800

TABLE V

Projective Area of Developable Grains per Class, in μ^2

Step No.	Mean Class Size 0.115	0.3	0.5	0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.1	Exp. in ergs
1	8.95	50.07	40.30	21.44	7.76	3.45		0.76	1.50	0.34	0.37	150
2		72.58	73.03	30.44	13.10	4.79	1.80	1.26	”	”	”	212
3	4.03	118.46	109.79	35.06	13.90	5.74	1.43	2.13	”	”	”	300
4	16.58	196.52	135.36	39.04	14.17	5.82	2.19	”	”	”	”	424
5	47.72	292.28	148.47	40.40	14.43	6.07	”	”	”	”	”	500
6	81.80	337.36	153.69	40.73	14.81	”	”	”	”	”	”	348
7	113.80	357.47	157.29	41.23	14.97	”	”	”	”	”	”	1200
8	130.23	366.79	158.26	”	”	”	”	”	”	”	”	1596
9	140.41	375.28	158.88	”	”	”	”	”	”	”	”	2400
10	146.17	380.62	158.99	”	”	”	”	”	”	”	”	3392
11	150.00	382.50	”	”	”	”	”	”	”	”	”	4300

The results of multiplying the areas of developable grains by these ratios are shown also in Fig. 3 (as continuous lines) and the ratios are inserted above the curves.

In this connection we should like to mention some curious phenomena which were observed while making the photomicrographs of developed and undeveloped grains. The first and third columns of pictures in Fig. 4 show certain grains before and the second and fourth columns the same grains after development. Notice that some grains which are together, separate in developing, others where the grains appear widely separated grow together. Other single grains are completely distorted. Cases have also been noticed, particularly with minute grains, where they either become smaller or disappear altogether in development.

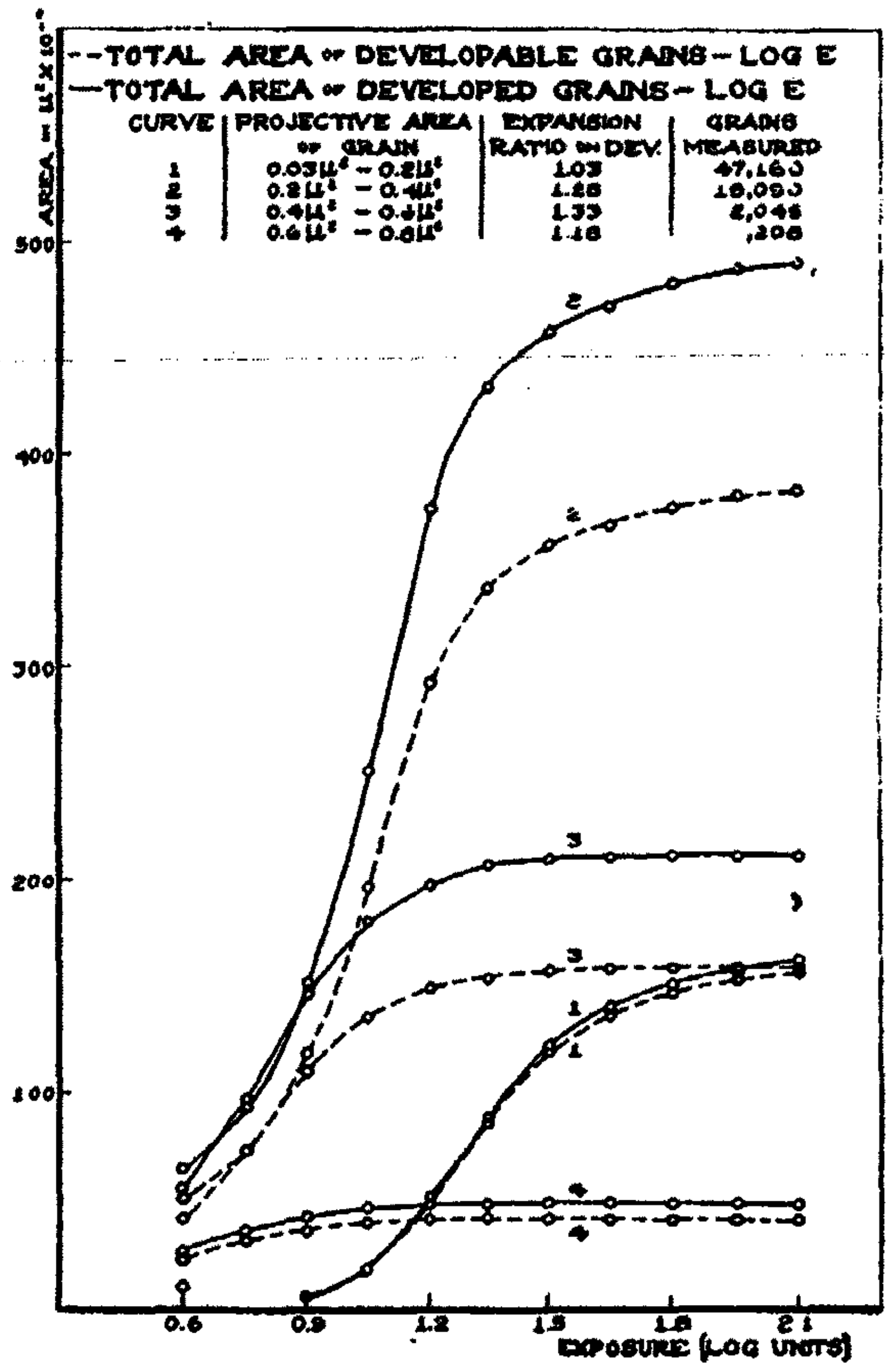

FIG. 3

The assuming of odd shapes is no doubt due to uneven strains in the surrounding gelatin. That is, as the spongy silver is formed the strains in the gelatin relieve themselves and push it (the silver) in the direction of least resistance. The disappearance of the more minute grains can be explained as due to their solution by the developer—with perhaps deposition elsewhere on larger grains.

Returning now to the subject of the conversion of the area-exposure curves. The curve of the first class-size is seen to fall completely out of consecutive order due to the fact that the frequencies of the first and second classes are nearly the same, while the grains of the second class average three times larger than those of the first. Curves for classes larger than the fourth

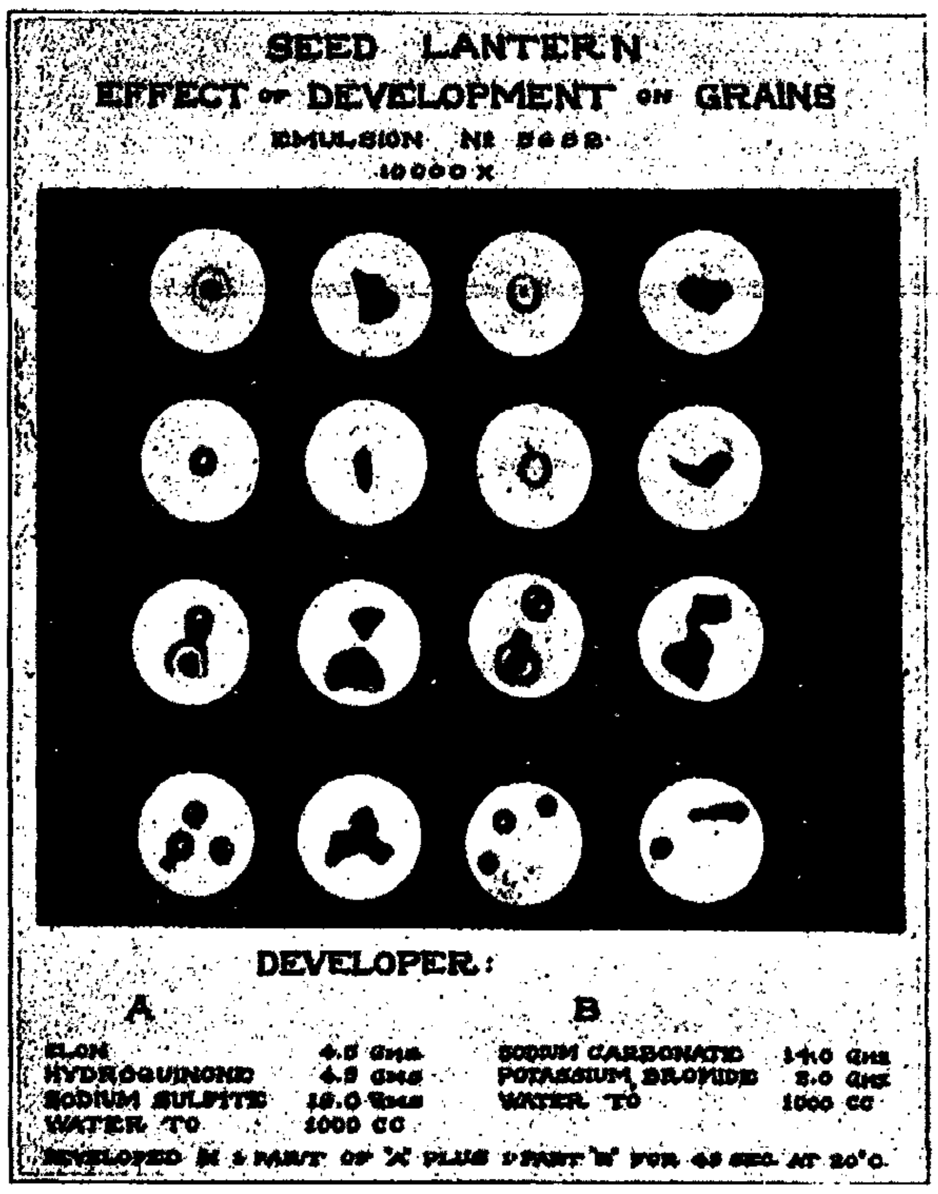

FIG. 4

have been omitted because of the difficulty of getting accurate expansion ratios for these in an emulsion with such a sharp maximum and narrow spread: that is, the number of grains of larger size occurring in the considerable number of micrograms made, is so small as to make the values of areas and expansion ratios very uncertain.

Nutting has stated[1] that the probability of light being stopped by solid silver grains lying in one layer on unit area of a photographic plate is the ratio of the covered to the total area, namely, of the number of grains, *n*, times their average projective area, *a*, to 1. Similarly, the probability of a ray passing the

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[1] P. G. Nutting: Phil. Mag., 26, 421 (1913).

layer of grains, is $1-na$. "In other words the absorption and transmission *coefficients* are respectively the *probabilities* of light being stopped and of being passed."

But a is of course equal, for any class size of grains, to the average area, x, of the original undeveloped silver halide grains in that class, times the expansion ratio of the developed to undeveloped grains, r. Hence, denoting transparency by T

$$T = 1 - nrx$$

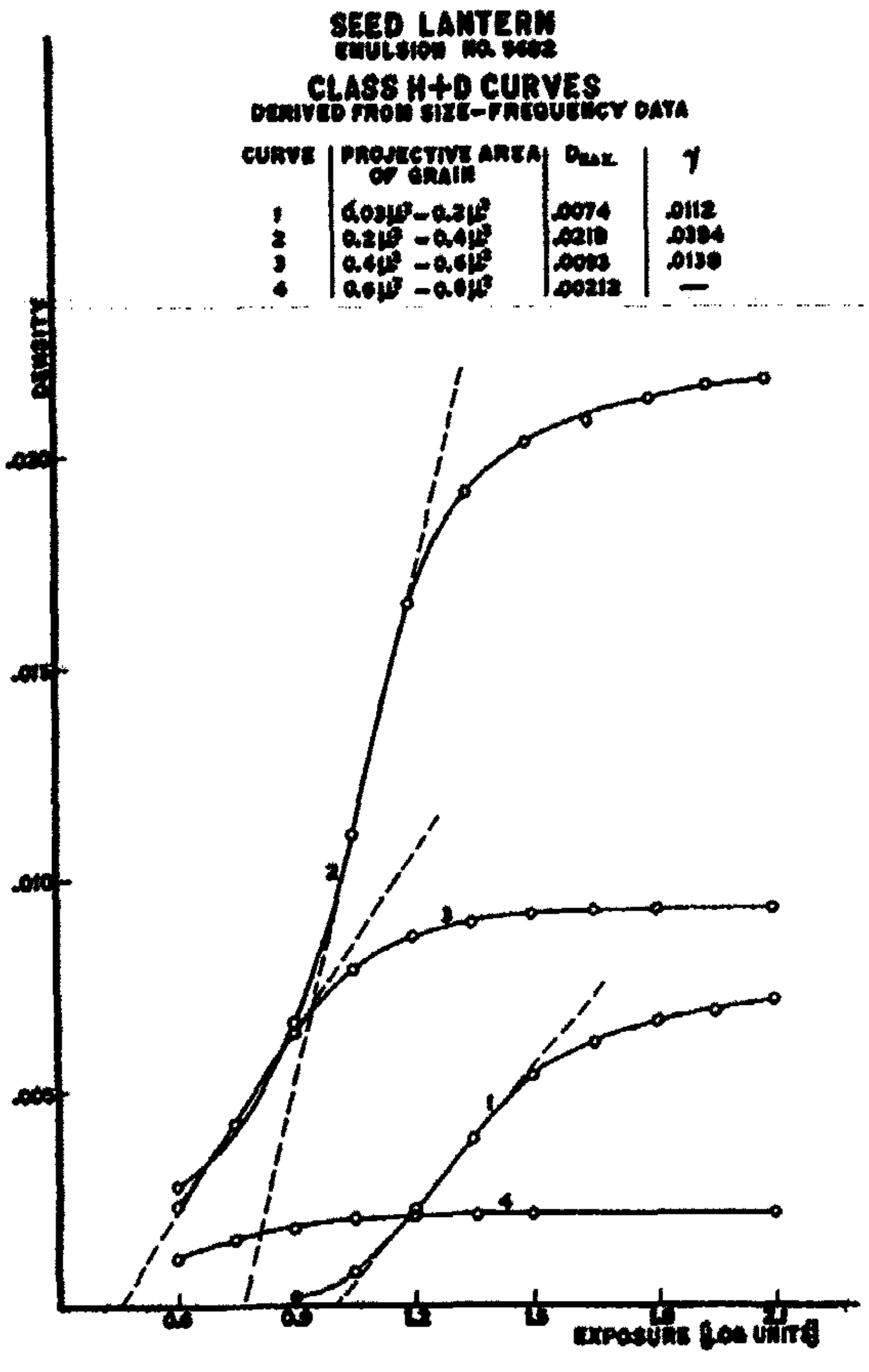

FIG. 5

Photographic density was defined by Hurter and Driffield[1] as

$$D = -\text{Log}_{10} T$$

For the individual classes of grains per unit area of a 1-grain layer plate we therefore have

$$D = \text{Log}_{10} \frac{1}{1 - nrx} \qquad (6)$$

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[1] F. Hurter and V. C. Driffield: J. Soc. Chem. Ind., 9, 455 (1890).

The values calculated by means of this formula (See Table VI.) are plotted in Fig. 5.

To form the composite density curve, in which the grains of all classes are mixed, we do not add the individual densities for each class size but make use of the formula

$$D = \mathrm{Log}_{10} \frac{1}{1-(n_1 r_1 x_1 + n_2 r_2 x_2 + \cdots + n_n r_n x_n)} \qquad (7)$$

where the letters have the same significance as in (6) and the subscripts indicate the class number. The resulting curve is shown in Fig. 6 as "curve B = synthetic H. and D." (for data see Table VI.).

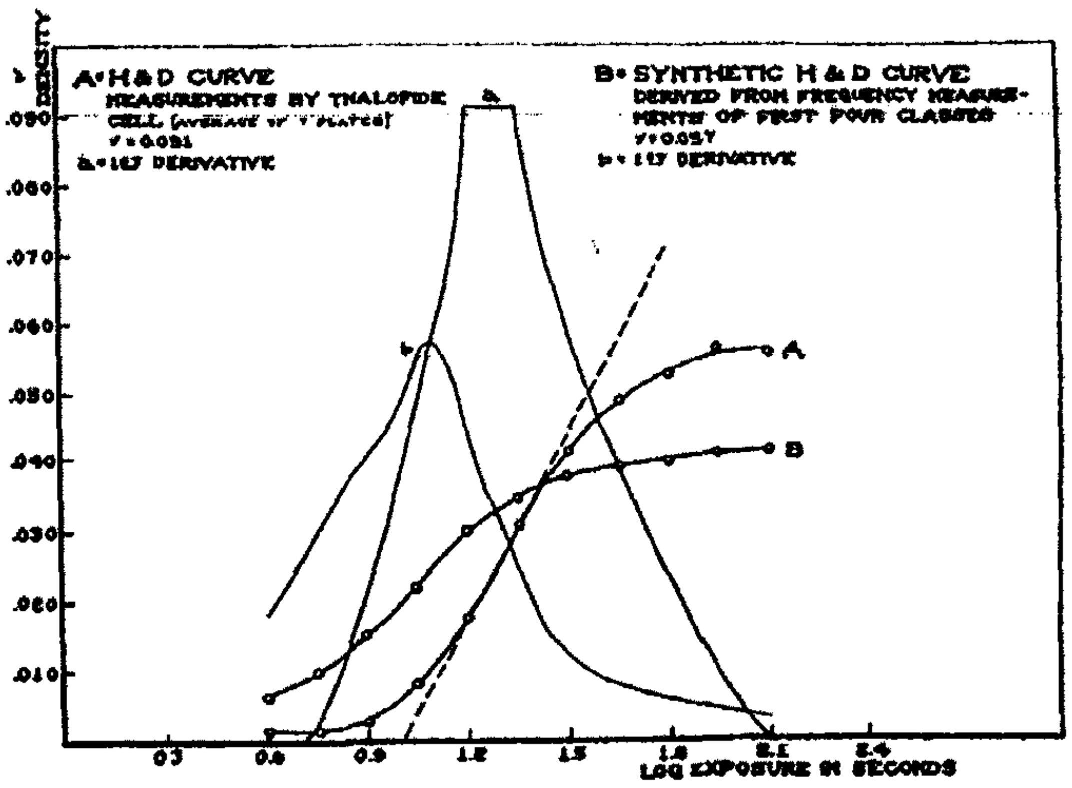

FIG. 6

We have given, for comparison, also the curve of densities against Log_{10} E for a similar set of plates measured by means of the thalofide cell densitometer (Curve A, Fig. 6). The two curves do not fit. This may be due to one or all of three causes:

1. The expansion ratios were determined only for the first four classes and were based on a comparatively few measurements in class four. Their accuracy is therefore questionable.

2. The density at any exposure may not be truly represented either by the formula by means of which the thalofide cell measurements are calculated, or

3. By the thalofide cell method itself.

These points are to be tested by further experimental work.

TABLE VI

Density-Log E Values

Step No.	Log E	Individual Class Densities				Synthetic H. & D. Composite	Measured H. & D. by Thalofide Cell
		1	2	3	4		
1	2.176		.00279	.00233	.00110	.00625	.0011
2	2.326		.00405	.00424	.00156	.00992	.0011
3	2.477	.00019	.00663	.00639	.00180	.01517	.0025
4	2.627	.00078	.01106	.00789	.00201	.02206	.0080
5	2.778	.00222	.01656	.00866	.00208	.03015	.0175
6	2.928	.00389	.01917	.00898	.00209	.03491	.0309
7	3.079	.00535	.02034	.00918	.00212	.03801	.0415
8	3.229	.00613	.02088	.00924	.00212	.03948	.0488
9	3.380	.00662	.02138	.00928	.00212	.04055	.0526
10	3.530	.00689	.02160	.00928	.00212	.04118	.0562
11	3.681	.00712	.02180	.00928	.00212	.04155	.0556

Summary

1. The size-frequency distribution of a Seed Lantern emulsion has been determined, and it was found that neither the simple exponential nor the Gaussian type of equation would fit it.

2. A more satisfactory equation was found which fits very accurately.

3. This equation

$$y = Ae^{-k(\ln x - a)^2}$$

results from the assumption that the growth of the particles in the emulsion is proportional to their size (surface or less accurately, their projective area) at any moment.

4. The formation of a photographic emulsion on the basis of this assumption seems to be a very reasonable one and we accept it as true for a number of cases.

5. It is shown why an equation of the same fundamental form (but not those used previously by us) can be used to represent both uniform diameter and uniform projective area classification.

6. A method of determining density values from size-frequency data was worked out and consists in converting the size-frequency to projective area distribution. Then, by applying a factor for the increase in size of the silver halide grain on development, the area distribution of developed grains is found, and finally the composite density D is calculated by means of the equation

$$D = \log_{10} \frac{1}{1 - (r_1 n_1 x_1 + r_2 n_2 x_2 + \cdots + r_n n_n x_n)}$$

where r_1, r_2, etc., are the expansion ratios, n_1, n_2, etc., are the frequencies of grains of each class-size per unit area of plate, and x_1, x_2, etc., are the mean class sizes.

7. A comparison of the synthetic density curve found in this way, with the curve obtained by means of the thalofide cell densitometer shows poor agreement. Possible explanations of this are given.

Rochester, N. Y.
December 1, 1923.

THE QUANTITATIVE DETERMINATION OF REDUCTION PRODUCTS OF FREE NITRIC ACID SOLUTIONS: NAMELY—NITROGEN PEROXIDE, NITRIC OXIDE, NITROUS OXIDE, NITROGEN, NITROUS ACID, AND SALTS OF HYDROXYLAMINE, HYDRAZINE, AND AMMONIA.

19-918

BY LOWELL H. MILLIGAN

I. Introduction.

When free nitric acid solutions are reduced by action on metals or strongly-reducing metal salts, or by electrolytic means, the different nitrogen compounds which result may vary from nitrogen peroxide down to ammonium salts depending on the method and the conditions attending the reduction. In actual experiments it has been shown that the action of nitric acid on metals may yield various mixtures of the products: nitrogen peroxide (NO_2), nitric oxide (NO), nitrous oxide (N_2O), nitrogen (N_2), nitrous acid (HNO_2), and salts of hydroxylamine (NH_2OH) and ammonia (NH_3). Therefore a complete careful study of such reactions or other related problems involves accurate analytical methods for the quantitative determination of these substances.

But in addition to the compounds which have actually been found as reduction products of free nitric acid, a number of others might be formed in solution and their ultimate survival or decomposition would depend on circumstances. Salts are known which are formed from nitrohydroxylamic acid ($H_2N_2O_3$) and hyponitrous acid ($H_2N_2O_2$), although the free acids themselves decompose at once with the liberation of NO and N_2O respectively. Nitramide (NO_2NH_2), an isomer of hyponitrous acid, has been isolated in the free state as a solid, but its solutions are quite unstable and decompose readily into N_2O and water. Thus, while these substances may exist momentarily as transitional stages, they break up so rapidly that no analyses need be made for them in the final acid solution. However, dilute nitric acid solutions of hydrazine (N_2H_4) and hydronitric acid (HN_3) are quite stable, and if these substances were once formed it might be necessary to determine them.

Many investigators who have studied the reduction of nitric acid have only made partial analyses, and often the methods used are open to serious objections. Probably Freer and Higley[1], who studied the action of nitric acid on metals, used better methods than most of the others, but even their procedures and results leave much to be desired.

The present work was undertaken as the first step in what it is hoped will finally be a thorough study of the action of nitric acid on metals, and its reduction by electrolytic means. In this paper, the gases which may be given off

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[1] Freer and Higley: Am. Chem. J., 15, 71 (1893); 17, 18 (1895); 18, 587 (1896); 21, 377 (1899).

(nitrogen peroxide, nitric oxide, nitrous oxide and nitrogen) are discussed first; the method which was developed for the analysis of these gaseous mixtures is then described, and the results obtained when known samples were taken for analysis are given. The residual nitric acid solution is then considered, and methods of analysis are described for salts of hydroxylamine, hydrazine, and ammonia, for nitrous acid, and also for strongly-reducing metal salts. Results are given which were obtained with known samples. The effect of hydronitric acid on analyses for the other compounds is considered, although the determination of hydronitric acid itself is not discussed. The methods of analysis for the nitric acid solution are as general as it has been possible to make them, but it is conceivable that they may fail in the presence of interfering substances not considered here. If such cases arise, they will have to be met with modifications of these methods, or with special new ones.

II. Analytical Methods for Gaseous Mixtures of NO_2, NO, N_2O, and N_2.

1. *General Discussion.*

The accuracy of analytical methods designed for mixtures of different compounds depends first on the individual accuracy of the methods for each substance alone, and second on the mutual effect of the methods when used together or successively as the case may be. In the following paragraphs the first of these factors is taken up in a more or less general way for NO_2, NO, N_2O and N_2, together with a few of the properties of these gases and the methods which were used in this investigation to obtain them in a pure state.

(a) *Nitrogen peroxide.*

Nitrogen peroxide is a brown gas in equilibrium with nitrogen tetroxide according to the reaction:

$$2NO_2 \rightleftarrows N_2O_4.$$

At low temperatures N_2O_4 is a colorless liquid, but as the temperature is raised it becomes brown due to dissolved NO_2, and it boils at about +26°C. In contact with concentrated sulfuric acid, NO_2 is partially oxidized and partially reduced, nitrosylsulfuric acid and nitric acid being produced according to the reaction:

$$2NO_2 + H_2SO_4 = NOHSO_4 + HNO_3.$$

and this reaction forms the best method for its determination.[1] As long as the sulfuric acid is maintained concentrated, both products are stable and have low vapor pressures. The "nitrous nitrogen" (i.e., nitrogen in the nitrosylsulfuric acid) may be determined by a permanganate titration, and the "total nitrogen" may be calculated from measurement of the volume of nitric oxide evolved when a given volume of the acid is shaken with mercury in a nitrometer. When the sulfuric acid has absorbed pure NO_2, the nitrous nitrogen is half the total nitrogen.

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[1] Lunge: Ber., **15**, 488 (1882); Lunge and Berl: Z. angew. Chem., **19**, 809, 858 (1906); **20**, 1714 (1907); Sanfourche: Bull. **31**, 1248 (1922).

For use in this work, nitrogen peroxide was prepared by slowly dropping concentrated nitric acid on warm arsenious oxide[2] and filtering the evolved brown fumes through glass wool, drying them over P_2O_5 and condensing them in a double U tube cooled in ice-salt mixture. Purification was accomplished in the apparatus shown in Fig. 1, the stopcocks of which were lubricated with P_2O_5. B and G in the figure, are tubes containing P_2O_5 and glass wool, and M is a $CaCl_2$ guard tube to prevent backward diffusion of water vapor from the water suction pump applied at N. About half of the crude green distillate from the first condensation was distilled through ABC into D where it was condensed by cooling. It was oxidized by admitting pure oxygen under a pressure of 2-3 atmospheres at A, and shaking until the liquid had changed to a deep brown color. It was then allowed to stand under an oxygen pressure for two days with occasional shaking, and was finally distilled through G into H, the first distillate and the last portion of the liquid being rejected. A short capillary tube blown into a bulb L at one end and ground off perfectly flat at the other, was accurately weighed before being attached with DeKhotinsky cement to a similar ground capillary on the apparatus at K. This method of attachment prevented appreciable action of the corrosive NO_2 fumes on the cement. By manipulating the stopcocks I and J the air was displaced from the bulb and tubes, and then the bulb was cooled in a freezing mixture of alcohol and CO_2-snow contained in a Dewar goblet, until sufficient N_2O_4 was obtained in the bulb as a colorless liquid or solid. The bulb was then sealed off with a tiny blast flame, the capillary was detached by warming at K, and the cement was removed with a little alcohol. The bulb and the capillary were weighed, the weight of the sample being calculated after correcting the weights to vacuo. Bulbs containing known weights of nitrogen peroxide were used as samples for testing the accuracy of the analytical methods described in detail further on in this paper.

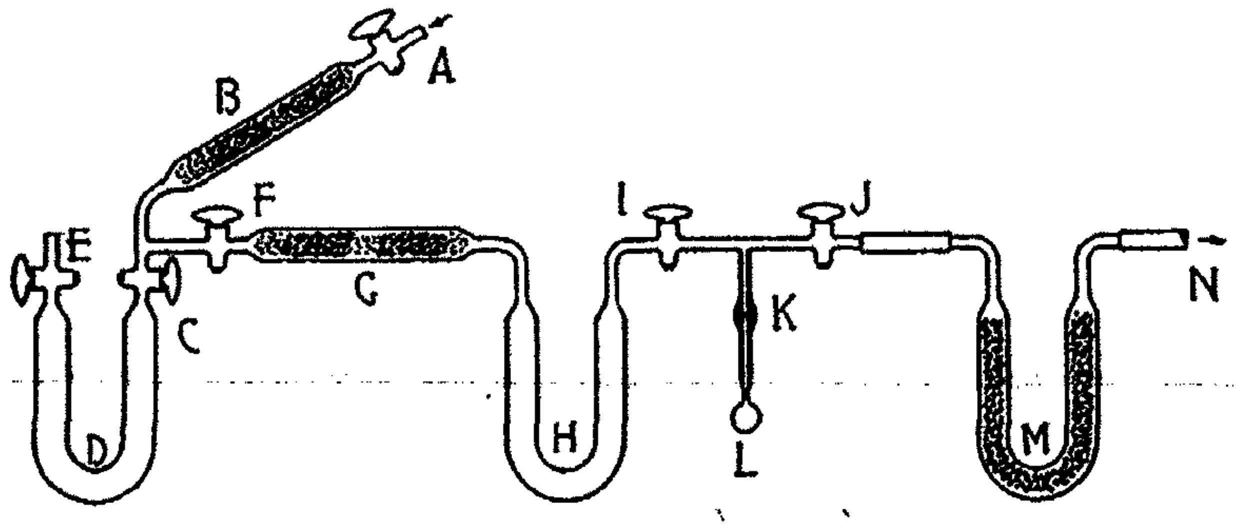

FIG. 1
Apparatus for the Purification of Nitrogen Peroxide.

(b) *Nitric oxide*

Nitric oxide is a colorless gas which readily combines with oxygen of the air to form nitrogen peroxide:

$$2NO+O_2 \rightleftarrows 2NO_2.$$

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[2] Hasenbach: J. prakt. Chem., (2) 4, 1 (1871).

Therefore analytical operations designed to separate NO and NO_2 must be carried out in the absence of air. Pure nitric oxide acts like an inert gas when it dissolves in pure concentrated sulfuric acid, in which it is quite insoluble[1]. In the presence of nitrogen peroxide, however, an equilibrium is set up:[2]

$$NO_2+NO \rightleftarrows N_2O_3.$$

and combination readily takes place with concentrated sulfuric acid to form nitrosylsulfuric acid and water:[3]

$$N_2O_3+2H_2SO_4=2NOHSO_4+H_2O.$$

Thus when pure N_2O_3 is completely absorbed by concentrated sulfuric acid, only nitrosylsulfuric acid (no nitric acid) is formed. The fact that Lunge and Berl found that absorption of an equimolecular mixture of NO and NO_2 in concentrated H_2SO_4 was not quite complete, and that the nitrous nitrogen in the acid was slightly less than the total nitrogen, is easily explained when the mechanism of the reaction is considered. Only a small amount of N_2O_3 is present at room temperature in a mixture of NO and NO_2, but the rate of combination between NO and NO_2 to form N_2O_3 is rapid up to the equilibrium point and the absorption of the N_2O_3 by the conc. H_2SO_4 is rapid, causing further formation of N_2O_3. However, NO_2 is absorbed alone in an independent reaction, and this takes place to a small extent with the formation of nitrosylsulfuric and nitric acids. If the nitric oxide which is thus left in the gases in excess, can come into contact with the nitric acid which is now present in the sulfuric acid, it will reduce it:[4]

$$HNO_3+2NO+3H_2SO_4=3NOHSO_4+2H_2O.$$

But all of the excess NO does not come thus into contact, and therefore a small amount of the NO escapes from the solution unchanged.

If concentrated sulfuric acid is used as an absorbing medium for NO_2 and mixtures of NO and NO_2, the relative amounts of NO and NO_2 which were absorbed can be calculated from determinations of the nitrous nitrogen and total nitrogen in the acid. However, if NO is present alone, or if there is a larger volume of NO than NO_2, other methods must be used to absorb it. In the first experiments made in this laboratory, a definite volume of 0.3 N permanganate solution acidified with sulfuric acid was used,[5] by means of which NO is quantitatively oxidized to HNO_3 when suitable precautions are taken to obtain good contact between the gas and the solution for measurable periods of time. At the end of the experiment the permanganate used up was calculated after adding a measured excess of standard ferrous sulfate solution and determining the excess by a permanganate back-titration. It was found,

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[1] Tower: Z. anorg. Chem., **50**, 382 (1906).

[2] Dixon and Peterkin: J. Chem. Soc., **75**, 613 (1899); Wourtzel: Compt. rend., **170**, 109 (1920).

[3] Lunge and Berl: Z. angew. Chem., **19**, 809, 858 (1906); **20**, 1714 (1907); Sanfourche: Compt. rend., **172**, 1573 (1921).

[4] This reaction is indicated by Freer and Higley (Am. Chem. J., **15**, 77 (1893). Sanfourche (loc. cit.) ascribes it to Lunge, but I have not been able to find it in any of Lunge's original papers. There is no question, however, but that it is accurate for concentrated H_2SO_4 containing a little nitric acid, as my work will show.

[5] See Moser: Z. anal. Chem., **50**, 422 (1911).

however, that oxides of manganese were precipitated when nitric oxide was absorbed by this solution, and they rendered accurate results impossible because they could not be washed satisfactorily from the absorbing vessel and they would not go completely into solution in the ferrous sulfate. Neutral permanganate solutions acted similarly. Experiments with addition agents designed to stabilize the permanganate, showed that phosphoric acid when used alone, completely prevented the precipitation of oxides of manganese by the nitric oxide. It was found, however, that these permanganate solutions gave off measurable amounts of oxygen, which was particularly unfortunate because it interfered with the determination of N_2O to be described in the next section of this paper. Phosphoric acid prevents the immediate precipitation of oxides of manganese from permanganate solutions, but it does not prevent them from giving off oxygen under certain conditions; nor does it prevent the eventual decomposition on standing, of standard permanganate solutions which are made with water containing small amounts of organic matter.

The final reagent which was found to be satisfactory for the absorption of nitric oxide, was concentrated (95%) sulfuric acid to every 100 cc. of which was added 2 cc. of concentrated (70%) nitric acid. This mixture absorbs NO with the formation of nitrosylsulfuric acid according to the reaction previously given, and the nitrous nitrogen in the acid, from which the NO is calculated, is afterward determined by a permanganate titration. The amount of NO which a given volume of this reagent is called upon to absorb, should always be considerably less than is equivalent to the nitric acid present.

Pure nitric oxide was prepared by shaking concentrated sulfuric acid containing a little nitric acid, with mercury.[1] Samples were measured by volume, over mercury in a moist burette.

(c) *Nitrous oxide.*

Nitrous oxide is a colorless, relatively inert gas which resembles carbon dioxide in many of its properties.[2] It is very soluble in most liquids, but does not form stable compounds with them, and may therefore be eventually "washed out" of solution in sulfuric acid, sodium hydroxide solutions, etc., by means of another gas.

The quantitative determination of nitrous oxide is often carried out by combustion with hydrogen, according to the reaction:

$$N_2O+H_2=N_2+H_2O.$$

The contraction on burning is equal to the volume of the N_2O. Such a combustion may be made in any one of three possible ways:

1. The N_2O may be exploded with hydrogen alone, or with hydrogen containing a known volume of oxygen.

2. The combustion with hydrogen may be made to take place slowly at a red-hot platinum surface, preferably a platinum wire in a "slow combustion" gas pipette.

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[1] See Moser: Z. anal. Chem., 50, 407 (1911).

[2] Langmuir: J. Am. Chem. Soc., 41, 1544 (1919).

3. The combustion with hydrogen may be carried out catalytically at a surface of warm. platinum or palladium asbestos.

The literature is full of conflicting statements regarding the accuracy of these methods.[1] Explosion with hydrogen tends to give low results, although many authors fail to make proper distinction between the various means of carrying out the combustion. Winkler advocates slow combustion with hydrogen at a red-hot platinum surface.[2] Kemp, however, finds ammonia in the products, and says that the method is unreliable. The low temperature combustion with warm. platinum or palladium asbestos can only be applied to analyses for small amounts of N_2O, because large and variable amounts of ammonia are formed under these conditions.[3]

Modern physical chemistry gives a rational explanation of the facts noted by the above observers. Haber[4] gives data on the equilibrium:

$$N_2+3H_2 \rightleftarrows 2NH_3.$$

At a total pressure of one atmosphere, 0.08% of NH_3 is present at 550°C., and 0.006% of NH_3 is present at 950°C. Therefore the combustion of N_2O with hydrogen should be carried out at a relatively high temperature in order to prevent appreciable formation of ammonia. At a red-hot platinum surface, even though ammonia may be formed by more or less localized low temperature reaction, it will be decomposed provided it comes again into contact with the hot surface before it is absorbed by the moisture in the pipette. This explanation also accounts for the fact that *nitric oxide* and hydrogen should be passed *slowly* through a red-hot platinum capillary if quantitative conversion to N_2 and H_2O is desired, as rapid passage causes the formation of appreciable amounts of NH_3.[5] Platinum or palladium asbestos is used at a comparatively low temperature, and under these conditions the equilibrium shifts toward larger quantities of ammonia, as various experimentors have found, although the conversion to ammonia is not quantitative.

Different investigators have tried to dissociate N_2O quantitatively into N_2 and O_2 by heating it alone,[6] but at high temperature NO tends to become more stable, because it is the most endothermic of the oxides of nitrogen. Appreciable amounts of it are produced according to the reaction:[7]

$$N_2+O_2=2NO,$$

and under these conditions the NO reacts with oxygen:

$$2NO+O_2=2NO_2.$$

In contact with water vapor which is always present, the nitrogen peroxide attacks the mercury which is used to confine the gases, and produces surface

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[1] Lunge: Ber., **14**, 2190 (1881); Kemp: Chem. News, **71**, 108 (1895); Hempel: Ber., **15**, 903 (1882); Dumreicher: Monat., **1**, 732 (1880); Baskerville and Stevenson: J. Ind. Eng. Chem., **3**, 581 (1911).

[2] Winkler: "Lehrbuch tech. Gasanalyse", 3d Ed., 190 (1901).

[3] Winkler: "Anleitung zur chemischen Untersuchung der Industrie-Gase", II, 429 (1877); Lunge: Ber., **14**, 2190 (1881).

[4] Haber: J. Soc. Chem. Ind., **33**, 53 (1914).

[5] Knorre and Arndt: Ber., **32**, 2138 (1899).

[6] Baskerville and Stevenson: J. Ind. Eng. Chem., **3**, 580 (1911).

[7] Haber: loc cit.

films which have been noticed experimentally. When the dissociation is produced in such a way that the oxygen is removed as an inert compound as fast as it is formed, then the N_2O can be quantitatively converted into nitrogen plus the inert oxide. This can be done actually by using an electrically heated iron wire, and has been used as a method for determining the atomic weight of nitrogen.[1] A similar case is the quantitative combustion of *hydrogen* by means of an *excess* of N_2O at low temperatures in the presence of palladium-black, according to the reaction:[2]

$$H_2+N_2O=H_2O+N_2.$$

The fact that low results are often obtained when N_2O is determined by explosion with excess hydrogen simply means that the combustion is not complete in these cases, because N_2O burns relatively slowly. The formation of *small* amounts of ammonia would be expected. It is therefore not surprising that Kemp often obtained a positive test with Nessler's solution on the residual gases from a combustion. His "deep yellow color" would probably not correspond to more than 0.1 mg. of nitrogen which, in itself, would introduce an almost negligible error in his results.

Thus the results of all the different workers with the exception of those of Kemp, who obtained "discordant" results by slow-combustion with hydrogen using a red-hot platinum spiral, can be explained on the basis of modern theory. Kemp's unsatisfactory results were probably due to impurities in the hydrogen or the nitrous oxide, to leakage or to other factors of which he did not take account.

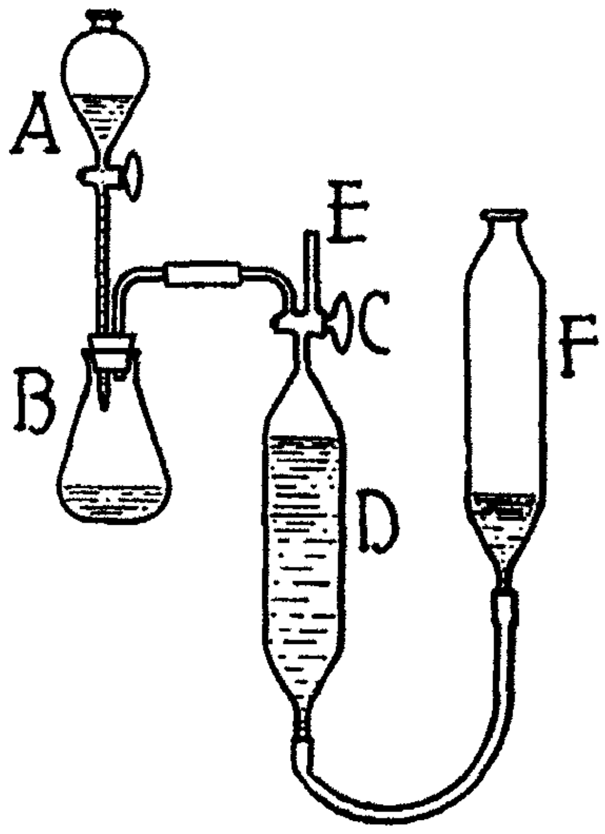

FIG. 2
Apparatus for the Preparation of Pure Nitrous Oxide.

In this laboratory it has been found that entirely satisfactory quantitative slow-combustions of nitrous oxide can be made with an excess of hydrogen, using a red-hot platinum spiral.[3] Pure nitrous oxide was prepared by the method of Victor Meyer[4], by allowing a fairly concentrated solution of *pure* sodium nitrite contained in the separatory funnel A, Fig. 2, to drop slowly on a concentrated hydroxylamine sulfate solution in B, causing nitrous oxide to be evolved:

$$2NaNO_2+(NH_2OH)_2H_2SO_4=Na_2SO_4+2N_2O+4H_2O.$$

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[1] Guye and Bogdan: Compt. rend., **138**, 1494 (1904); Jaquerod and Bogdan: ibid, **139**, 49 (1904).

[2] Montemartini: Accad. real. Lincei, **7**, II, 219; through J. Chem. Soc., **64** II, 113 (1893).

[3] Mr. George W. Jones, who is in charge of the gas laboratory of the U. S. Bureau of Mines Experiment Station at Pittsburgh, Pa., has told me that he also has found this method satisfactory.

[4] Meyer: Ann., **175**, 141 (1875).

The N_2O passed over into D where it was collected over water saturated with it. Air was thoroughly washed out of the apparatus by successive portions of N_2O before collecting any of the gas for use. The rate of addition of sodium nitrite solution was such that the solution in B, which was shaken during the addition of the nitrite, became only barely warm.

The preparation of pure sodium nitrite solution involved the intermediate preparation of silver nitrite. Five grams of C. P. $NaNO_2$ were dissolved in about 50 cc. of distilled water, and this was added slowly, with stirring, to a solution of 10 grams of $AgNO_3$ in 50 cc. of water, both solutions being made with cold water and used as soon as prepared. The precipitated $AgNO_2$ was filtered by suction, washed once with ice-cold distilled water to remove the excess $NaNO_2$, and then transferred to a beaker. A solution of 4 grams of C. P. NaCl (this is a small excess) in 25 cc. of water was added to the precipitate with stirring, thus converting the $AgNO_2$ into AgCl, and forming pure $NaNO_2$ in solution, together with the slight excess of NaCl which does no harm. This solution was filtered and placed in A. The solution in B was a strong solution of Kahlbaum's hydroxylamine sulfate. This method gives pure N_2O, and has been used for the preparation of pure gas for density determinations and for atomic weight work.[1]

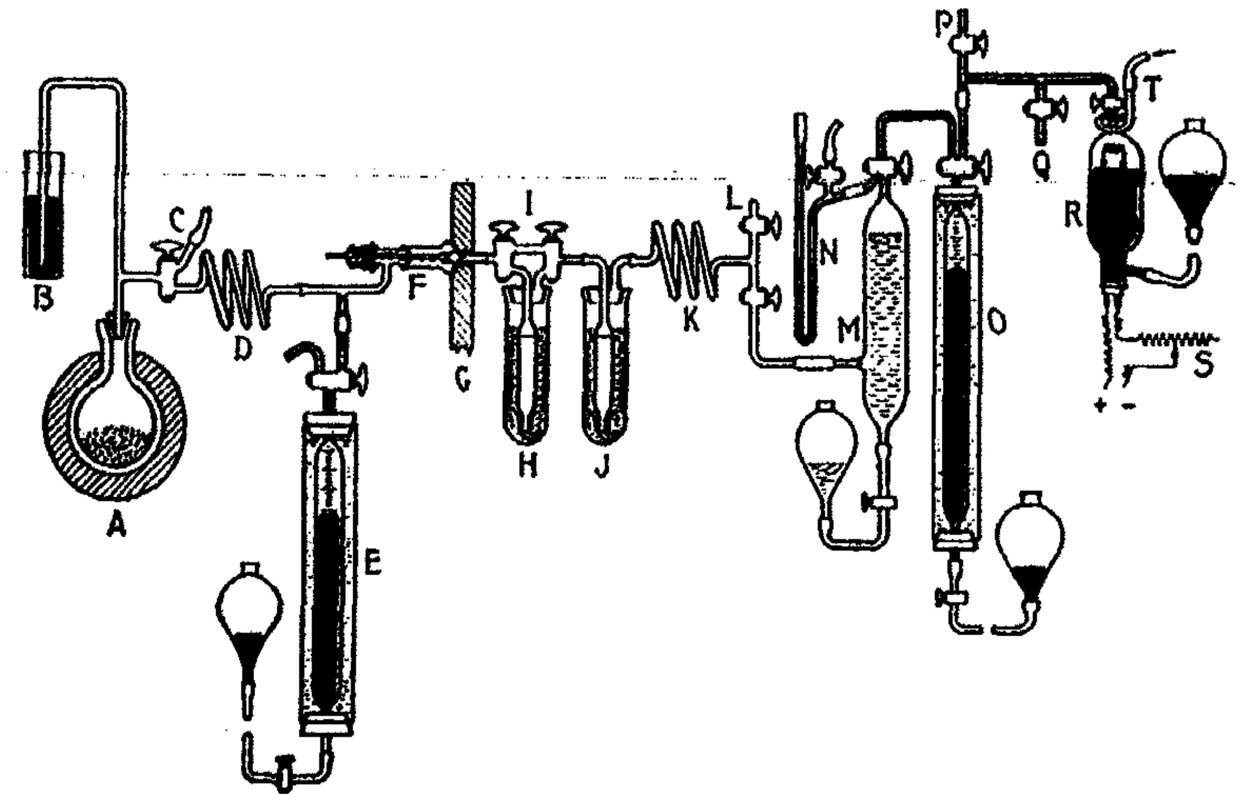

Fig. 3

Apparatus for the Analysis of Gaseous Mixtures of NO_2, NO, N_2O, and N_2, showing the way in which known amounts of the gases were introduced in order to test the accuracy of the method.

The combustions were carried out in the apparatus shown in Fig. 3, from N to T, and the manipulation was as is described in detail for the combustion of the residual gas from an actual run (p. 559), except that the sample of purified hydrogen was measured and transferred to the combustion pipette and then the pure N_2O was introduced at P into the gas burette. The first

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[1] Guye and Bogdan: Compt. rend., 138, 1494 (1904): Jaquerod and Bogdan: 139, 49 (1904).

5 cc. of the N_2O were used to wash the hydrogen out of the capillary, and were vented to the air out through the stopcock attached to N. The sample used for combustion was then drawn into the burette and measured. In calculating the results, the volume of the capillary (0.2 cc.) which contained N_2O and not H_2, was subtracted from the volume of the hydrogen actually measured in the burette, and was added to the measured volume of N_2O. The corrected results are given in Table I.

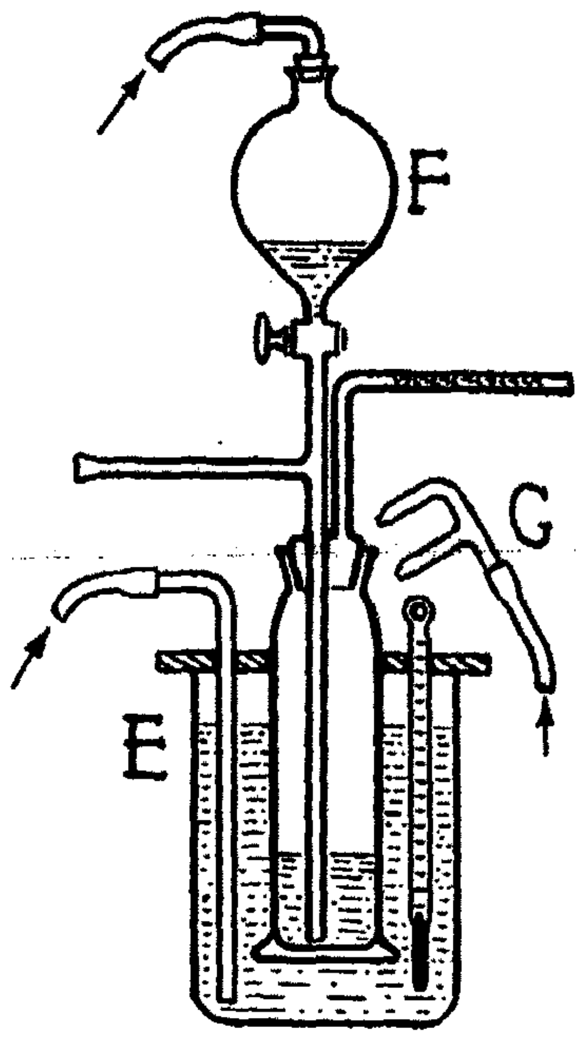

Fig. 3a
Reaction Bottle for carrying out Reductions of Nitric Acid (in use this is substituted for E, F, and G in Fig. 3).

(d) *Nitrogen*

The preparation and determination of nitrogen presents no difficulties in this work. It was very simply prepared by shaking an air sample with alkaline pyrogallol solution in a double Hempel absorption pipette until the oxygen was completely removed from the air. The analysis for nitrogen is made by collecting and measuring it together with the nitrous oxide, determining the nitrous oxide by combustion with hydrogen, and calculating the nitrogen by difference.

2. *The Analysis of Gaseous Mixtures of NO_2, NO, N_2O and N_2.*

The apparatus developed for the analysis of gaseous mixtures of NO_2, NO, N_2O and N_2, is shown in Fig. 3. These gases are conveyed with pure carbon dioxide obtained by allowing CO_2-snow to evaporate. The snow is contained in a 1-liter unsilvered Dewar flask surrounded with a cotton jacket, shown at

Table I

The Analysis of Pure N_2O by Slow-Combustion with Hydrogen.

Determination No.	1		2		3	
Pure H_2 taken, cc.	66.8		68.8		51.8	
" N_2O " "	19.6		25.7		14.8	
Total volume, cc.		86.4		94.5		66.6
After 1st burn, cc.	68.1		69.8		53.0	
" 2nd " "	66.9		68.8		51.8	
" 3rd " "		66.9		68.8		51.8
N_2O found, cc.		19.5		25.7		14.8
Error, cc.		−0.1		0.0		0.0

A. B is a bottle filled with mercury, which regulates the pressure on the system, and through which the excess carbon dioxide escapes. The glass spirals D and K are introduced to obtain flexibility in making the joints, which are mostly of the cup and cone variety, and are sealed gas-tight with DeKhotinsky cement. E and F serve to introduce known amounts of the gases. The absorption train proper starts at bottle H, which contains concentrated sulfuric acid for absorbing NO_2 (and NO in the presence of NO_2) and is fitted with a by-pass I. Bottle J contains concentrated $H_2SO_4-HNO_3$ reagent to absorb NO. M has a capacity of about 250 cc. and contains 20% NaOH solution for absorbing the carbon dioxide wash gas. The N_2O and N_2 collect in the top of this tube. The rest of the apparatus serves for the analysis of the residual gas (i.e., the N_2O and N_2) after the "run" is completed, and consists of a 100 cc water-jacketed burette O, a capillary water manometer N, and a Dennis slow-combustion pipette R, fitted with a variable resistance S and air-cooling device T. An electrolytic hydrogen generator is permanently connected at Q.

Any impurities introduced by the carbon dioxide will collect over the sodium hydroxide solution and introduce an error in the results of analysis of the residual gas. Preliminary experiments showed that CO_2 taken direct from ordinary tanks would not be of sufficient purity to serve. Dr. A. M. Erskine working in Prof. A. W. Browne's laboratory at Cornell, used CO_2-snow successfully as a source of pure gas, and his scheme was adopted and found satisfactory. A few experiments were made with carbon dioxide generated by the Bradley and Hale method[1] from the reaction between sodium bicarbonate and concentrated sulfuric acid, but it was found that the excess trouble and time required to operate their apparatus more than overbalanced any possible advantage due to slightly greater CO_2 purity. The average impurity in the gas from CO_2-snow was less than 1 part in 10,000 and was apparently nitrogen which was adsorbed on the snow itself.

The absorption bottles H and J have a capacity of 100-150 cc., and are of special design in order to overcome difficulties experienced with the ordinary, non-circulating type of Friedrichs' bottles[2] which are available in this laboratory, but which fail to circulate the liquid adequately. In the ordinary Friedrichs' bottles, the spiral is made of thin glass, the inside of which serves as the gas inlet and contains a series of deep V-shaped grooves from which the air or gas is only slowly displaced. The new bottles,[3] shown in detail in Fig. 4, have proven entirely satisfactory. A straight gas-inlet tube was sealed on in place of the spiral, the spiral itself was cut off straight across the top and the bottom, and was slid over this inlet tube, and the bottom end of the tube was turned up to hold the spiral on. When this bottle is in use the spiral is completely submerged in the liquid which circulates continuously up with the gas between the spiral and the inside of the bottle, and then

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[1] Bradley and Hale: J. Am. Chem. Soc., 30, 1090 (1908).

[2] Friedrichs: Z. anal. Chem., 50, 175 (1911).

[3] Patent application has been filed covering the new features of these bottles.

down between the spiral and the central tube. There can be no trapping of the gas because the inside tube through which the gas enters is perfectly straight. The tops of these bottles are accurately ground and are "sealed" by moistening the ground surfaces with a tiny drop of concentrated sulfuric acid. The bottles are held together against the gas pressure by twisted copper wire and rubber band, as shown in Fig. 4. Tests showed that one of these special bottles filled with reagent gave complete absorption of NO_2 or NO under all conditions of use in the apparatus.

Before starting a run, portions of the acid are measured into the dry absorption bottles with a 50 cc. pipette. This will not deliver quite 50 cc. of conc. H_2SO_4, but after the run is over, a 25 cc. pipette is used to measure out aliquots of the acid for analysis, and the ratio of acid delivered by the 50 and 25 cc. pipettes is 2:1 within 1 or 2 parts in 1000, which is satisfactory. A 10 cc. pipette was sometimes used after the run, and it was found that the ratio of acid delivered by the 50 and 10 cc. pipettes was 5.02:1, and this ratio was applied in the calculations.

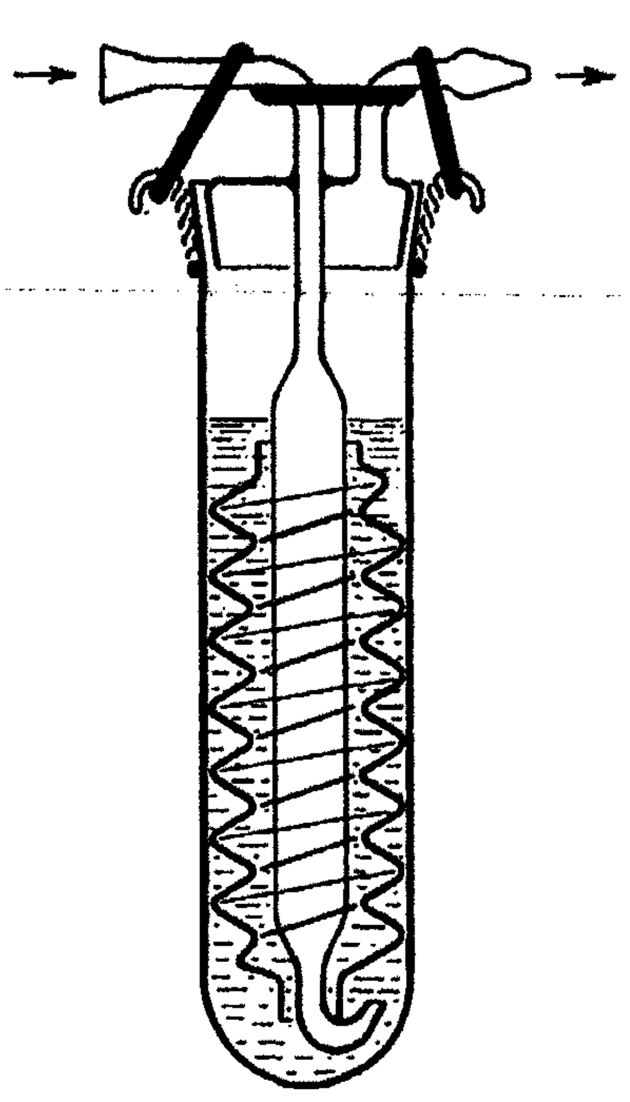

Fig. 4
The Modified, Spiral, Washing-Bottle.

After the run, the nitrous nitrogen in the acid from each bottle is determined by a permanganate titration. It is not possible to dilute the acid and titrate it directly because such procedure would result in a loss of NO set free when the $NOHSO_4$ is destroyed by dilution with water, and also because the permanganate end point is not sharp under these conditions. It is satisfactory, however, to dilute a measured, excess volume of the standard $KMnO_4$ solution with a very large amount of water (say 800 cc.) and then add a pipette of the acid with stirring, keeping the tip of the pipette submerged during the addition. An excess of permanganate should always be present. If oxides of manganese precipitate, another determination should be made, adding 10 cc. of syrupy phosphoric acid to the diluted permanganate in order to prevent this decomposition. A measured volume of standard ferrous sulfate solution, which should be of slightly greater strength than the permanganate and should contain free sulfuric acid, is then added and the excess back-titrated with permanganate. A blank determination on a pipette of pure conc. H_2SO_4 is made in exactly the same way, using the same volume of ferrous sulfate, and the difference between the determination and the blank represents permanganate used in oxidizing the nitrous nitrogen in the sample. The blank will not, in general, have quite the same value as a direct comparison of the permanganate and ferrous sulfate made in the usual way, because the addition of the concentrated sulfuric acid will decompose a small amount of the permanganate, but should not deposit visible oxides of manganese.

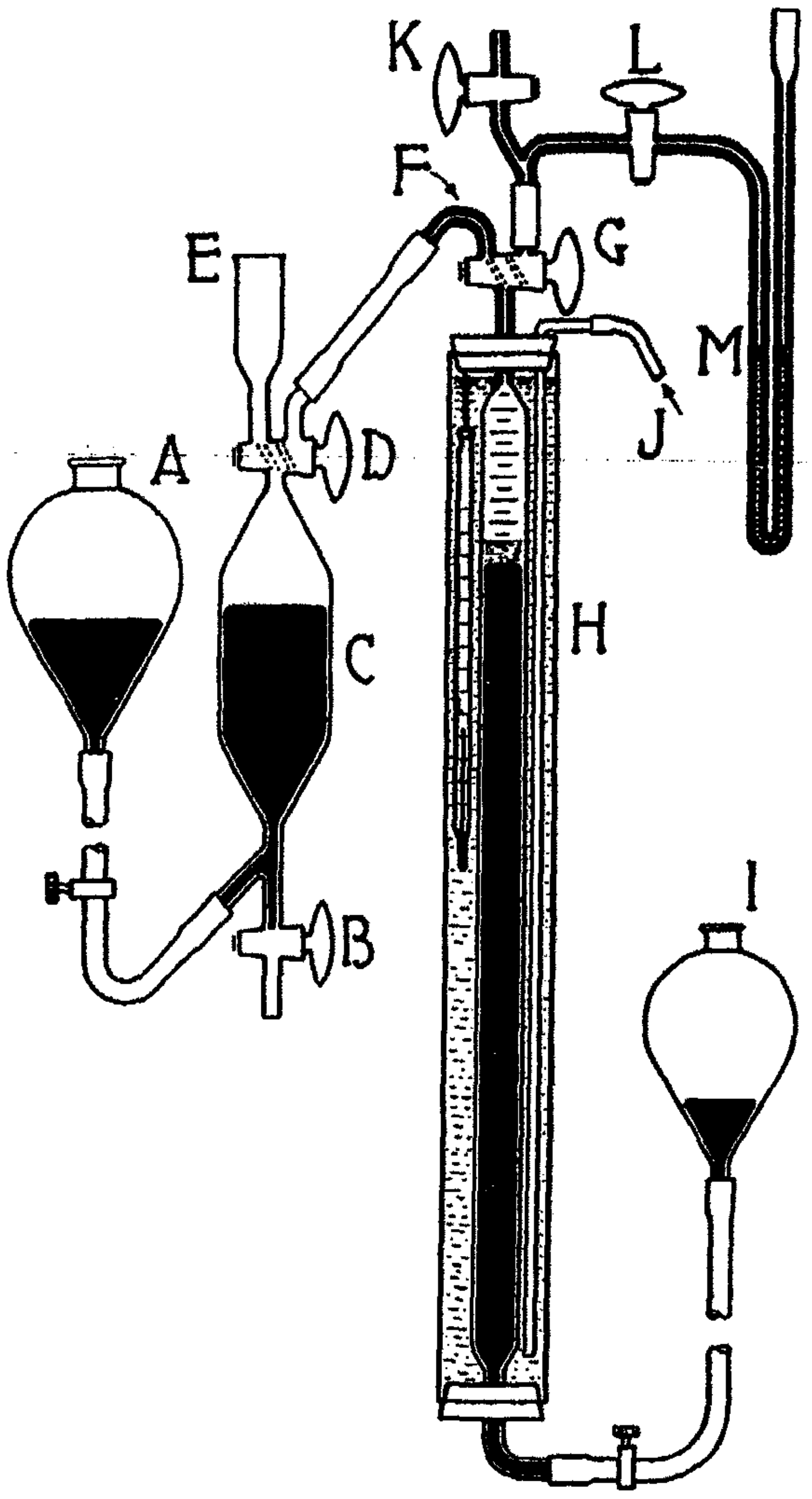

FIG. 5
The Nitrometer for determining the Total Nitrogen collected in the Concentrated Sulfuric Acid of the First Absorption Bottle.

Fig. 5 shows the nitrometer used for determining the total nitrogen collected in the sulfuric acid of the first absorption bottle. C is a tube of about 125 cc. capacity in which the reaction with the mercury takes place. The cup E has a capacity of about 10 cc., and is used for introducing the sample. The cock B is used for draining out the spent acid at the end of a determination. H is a 50 cc. gas burette graduated in 0.1 cc. and calibrated from the point F to contain gas over a water meniscus. J is a tube for bubbling agitating air through the water jacket. M is a capillary water manometer.

The first determinations of the total nitrogen in the sulfuric acid from the first absorption bottle were not satisfactory. This could be ascribed to several causes:

1. The acid was saturated with carbon dioxide which was washed out in the nitrometer by the liberated NO, giving high results. Attempts to remove the CO_2 by evacuation were unsuccessful because a poor vacuum did not remove all the CO_2, while a good one removed some of the nitric acid too. The difficulty was overcome by placing 1 cc. of 10% NaOH solution over the mercury in the nitrometer burette, and then passing the gases slowly back and forth five or six times between the tube and the burette before measuring the volume of the NO. This serves to absorb the CO_2 completely. Tests showed that the volume of NO absorbed under these conditions could not be detected i.e., was less than 0.03 cc. The 10% NaOH solution has a vapor pressure which averages about 1 mm. less than pure water at room temperature, and this should be taken into account when calculating the aqueous tension in the gas.

2. The results were irregular due to the variable solubility of NO in concentrated H_2SO_4 containing different amounts of Hg_2SO_4. Tower has shown[1] that concentrated sulfuric acid should not be used for nitrometer determinations because nitric oxide is not only much more soluble in it than in slightly diluted acid, but its solubility is variable, depending on the amount of dissolved mercurous sulfate, which may be considerable in the concentrated acid. Acid weaker than 90% gives satisfactory results because Hg_2SO_4 is not sufficiently soluble in it to affect the solubility of the NO. A constant correction for the solubility of the NO in the acid can then be introduced.

An attempt was made to use 87% sulfuric acid as the absorbent for nitrogen peroxide, but it failed because the solution rapidly lost nitric acid. This would be expected because Saposchnikow has shown[2] that dissolved nitric acid in sulfuric acid weaker than 90%, exerts an appreciable vapor pressure.

This trouble was finally avoided by using concentrated (95%) sulfuric acid as the absorbent, taking pains to protect it even from water vapor in the air, but washing the sample into the tube of the nitrometer with 5 cc. of dilute sulfuric acid of such strength that when mixed with the sample the final acid has a strength of 88% H_2SO_4. For a 25 cc. sample the proper strength of dilute acid is prepared by mixing 100 cc. of conc. (95%) H_2SO_4 with 243 cc. of water, and cooling to room temperature.

The constant correction for the solubility of NO in the sulfuric acid can be calculated from Tower's data, which indicates that 0.0193 cc. of NO will dissolve in 1 cc. of 90% H_2SO_4 at 18° C. and 760 mm. of NO pressure. This gives

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[1] Tower: Z. anorg. Chem., 50, 382 (1906).

[2] Saposchnikow: Z. phys. Chem., 49, 699 (1904); 53, 226 (1905).

0.58 cc. as the solubility correction for a 25 cc. sample with 5 cc. of wash acid. Actual determinations, using known weights of twice-crystallized C. P. KNO_3, were made in order to check this, because it was thought that the heat liberated in the nitrometer might be sufficient to change it appreciably. It was found, however, that the volume of NO produced, as compared to that calculated from the weight of KNO_3 taken, from several determinations gave an average of almost exactly Tower's figure, which is therefore assumed to be correct for this work.

3. The capillary water manometer shown at M in Fig. 5, is used as a delicate indicator of the proper adjustment of the mercury bulb I for bringing the NO in the burette to exactly atmospheric pressure. However, the capillary tube KG contains air, and when the stopcock G is turned so as to open into this capillary, a little of the NO in the burette is oxidized to NO_2 by the oxygen in this air; the NO_2 is absorbed by the caustic solution in the burette, and a diminution in volume occurs, causing appreciable error. This is avoided by filling the capillary with nitrogen just before starting each determination.

The nitrometer is prepared for use by filling the tubes between C and H with mercury, and bringing the mercury just through the stopcock into the cup E. A funnel is attached at K, the bulb I is raised until the mercury in the burette comes up into the funnel, a few cubic centimeters of 10% NaOH solution are poured in and the bulb lowered until about 1 cc. of the caustic solution has been drawn into the capillary and burette, after which the screw clamp on the burette hose is closed, the excess caustic poured out of the funnel, and the latter removed. A source of oxygen-free nitrogen is attached at K, about 5 cc. of nitrogen are slowly drawn into the burette (regulating with the screw clamp) and the nitrogen source is then removed. This nitrogen is slowly forced out of the burette until the level of the caustic comes just to the bottom of the stopcock G; then all the cocks are closed.

The acid sample is delivered from a pipette into the cup E, and simultaneously is drawn into the tube C, without getting any air in with it. The cup is washed with two 2.5 cc. portions of dilute sulfuric acid of the proper strength, and the tube is *vigorously* shaken, continuing the shaking for a minute after action seems to have ceased. The evolved gas is passed slowly back and forth between the burette and the tube about six times, and then the acid is carefully drawn up to the point F, and the stopcock G is closed. The mercury in the burette is leveled as closely as possible with the bulb I, and then final adjustment to atmospheric pressure is made by means of the capillary water manometer M, and the volume of the NO is read immediately.

The apparatus is cleaned by venting the NO out through K, sucking a sample of air into the burette and pushing the acid out of the capillary with part of it. The cock D is turned so as to open to the air, the mercury from the tube C is drawn into the bulb A, and the spent acid is run out through the cock B. The burette and the tube are then washed with successive portions of water introduced at K. It has been found advisable to use a straight vaseline-paraffin grease (without any rubber in it) for the stopcock G, which comes in contact with the caustic solution.

The relative amounts of NO_2 and NO absorbed in the first bottle are found from the analytical data as follows:

Let A = total nitrogen found in the first bottle.
B = nitrous " " " " " " .
x = nitrogen in the NO_2 absorbed.
y = " " " N_2O_3 " .

Then, from the reactions which take place on absorption of the gases (pages 545 and 547)

$$A = x + y. \qquad B = (0.5)x + y.$$

Therefore:

$$NO_2 \text{ absorbed} = \frac{2NO_2}{2N}x + \frac{NO_2}{2N}y = (3.285)x + (1.642)y.$$

$$NO \text{ absorbed} = \frac{NO}{2N}y = (1.071)y.$$

The total NO is the sum of that found by this calculation and that found in the second absorption bottle.

The by-pass I on the first absorption bottle (Fig. 3) is used only in cases where it is desired to analyse for nitrous acid by decomposing it completely, and discussion of the use of the by-pass will therefore be postponed until nitrous acid is considered further on in this paper.

Before beginning a run, it is necessary to pass carbon dioxide through the completely assembled apparatus (which must be tested each time to be sure that it is gas-tight) for about two hours in order to eliminate air. During this preliminary washing the gas is vented through the cock L. A purity test is made then by collecting the residual gas over the caustic solution for a definite short period of time (say three minutes) at a constant rate governed by the rate of absorption of the carbon dioxide and determined by closing the screw-clamp at the bottom of the tube M when the level of the caustic solution has been brought by the carbon dioxide stream to the point shown in Fig. 3. At the end of this time, the stopcock between K and M is closed, the screw-clamp is opened, and the approximate volume of the unabsorbed gas residue is estimated. When successive determinations show that this has reached a value which has been previously found satisfactory, the run is begun.

Nitrogen is only very slightly soluble in the absorbing liquids used, and a given volume of it can therefore be washed through with the carbon dioxide stream without appreciable loss. Nitrous oxide, on the other hand, is very soluble and even after maintaining the carbon dioxide stream for three hours (which was chosen as the proper period of time for operation) it is necessary to add 2 mg. to the weight of the N_2O found in order to correct for N_2O which is not washed out of solution in the absorbing liquids. This marks the approximate limit of *sensitivity* of the method for N_2O. It is also necessary to correct the volume of the residual gas for 0.7 cc. of nitrogen, which represents the volume of the impurity in the carbon dioxide passed through for three hours at a rate corresponding to 60–70 bubbles per minute in the caustic solution during the first hour, and 90–100 during the second and third (a total carbon dioxide volume of approximately seven liters).

When the caustic solution is prepared, the heat generated drives practically all the air out, and it can be kept air-free for quite a few days in a stoppered bottle. During the run, if considerable amounts of residual gas tend to build up in M and displace the caustic solution, portions of the residual gas can be withdrawn from time to time into O for storage. However, before this is done for the first time, the capillary tube between M and O should be evacuated by using the mercury in O as a pump. At the end of a run, it was originally thought necessary to evacuate the space over the caustic solution in order to pump out the nitrous oxide, but this was found useless because no appreciable amounts remained dissolved in the caustic solution. The *rate* of solution of nitrous oxide in the caustic solution is very slow, and it is therefore possible to take the residual gas immediately at the end of a run and remove all the carbon dioxide from it without absorbing appreciable amounts of N_2O, by passing it between M and O with intermediate short periods of rest in M. The volume of the residual gas is then measured in O, using the capillary water manometer N to aid in bringing it exactly to atmospheric pressure. The total volume read in the burette must, of course, be corrected for the volume of the capillary between M and O.

The analysis of the residual gas is carried out as follows:—The residual gas is stored in M for a few moments while a sample of hydrogen is drawn into the burette from Q. This is purified by passage back and forth over the red-hot platinum spiral in R, and about 70 cc. of it (or two and a half times the volume of the residual gas sample) are brought to atmospheric pressure, accurately measured, and then stored in the combustion pipette. About 30 cc. of the residual gas are accurately measured at atmospheric pressure, the screw-clamp on the rubber hose of the burette is closed, the mercury bulb is raised to its highest position, the stopcocks are opened between O and R, and the platinum spiral is heated to a *bright* red. The screw-clamp is then just barely opened, so as to feed the sample into the hydrogen at an extremely slow rate—so slow that the movement of the mercury in O can only just be seen—and the variable resistance S is slowly increased during the addition so as not to overheat the glower. When the sample is all in, the gases are passed slowly back and forth once or twice and then measured, not by bringing them to atmospheric pressure, but simply by bringing the mercury bulb to a definite position. Then the gases are passed slowly a few times more over the red-hot spiral and the volume read again with the mercury bulb in the same position as before. This is repeated until no more contraction takes place on burning, after which the gases are brought to exactly atmospheric pressure and their volume read. If the thermometer or barometer has changed appreciably since the first reading, the volume is corrected to the original temperature and pressure, and the contraction, which is equal to the volume of the N_2O present, is obtained by subtraction. The relative amounts of N_2O and N_2 in the total residual gas are calculated, and the volume of the N_2 is corrected for the impurity introduced by the CO_2 (i.e., 0.7 cc. is subtracted). The calculated weight of the N_2O is corrected for the weight of the N_2O which could not be washed out of the absorbing liquids (i.e., 2.0 mg. is added).

3. *Results obtained with Known Mixtures.*

In order to test the accuracy of the methods of analysis described for gaseous mixtures of NO_2, NO, N_2O and N_2, known amounts of these gases were taken as samples for analysis. The pure gases NO, N_2O and N_2 were measured by volume in the burette E, Fig. 3. A tiny glass bulb containing a weighed amount of NO_2 was placed in the tube F, which rests against the wooden support G. The glass plunger in F was slid through the rubber hose until it was just in contact with the bulb. After all the air had been displaced from the apparatus with carbon dioxide, the bulb containing the NO_2 was broken by a sharp blow against the glass plunger with a piece of wood. Known volumes of the other gases were introduced. The carbon dioxide stream was continued for three hours, and the analysis then completed.

The volumetric apparatus which was used, was either certified by the Bureau of Standards, or met their specifications[1] and was calibrated in this laboratory. The analytical weights were checked to 0.2 mg. by comparison with standards; the thermometers were selected so as to check to within 0.2°C. with a standard thermometer over the range used. The gas burettes were all supplied with water jackets containing a thermometer and a tube for admitting air for agitation. Atmospheric pressures were determined by means of a standard, high-grade mercurial barometer fitted with a vernier, and the readings were corrected to 0°C. The permanganate solution used for the determination of nitrous nitrogen in the sulfuric acid from the absorption bottles, was standardized against Bureau of Standards sodium oxalate[2]. Guye's "most probable" values for the weight of one liter of dry NO, N_2O and N_2 at N. T. P.[3], were used for volume-to-weight conversion factors.

Results are given in Table I. The accuracy of the methods indicated by this table has been substantiated by analyses of the gases produced by actual reductions of nitric acid in which known amounts of reducing agents were employed.

III. Analytical Methods for Nitric Acid Solutions which may contain Strongly-Reducing Metal Salts, Ammonium Salts, and Nitrous Acid or Hydroxylamine and Hydrazine Salts.

When a dilute solution of free nitric acid is partially reduced and the gases formed are washed out by means of a stream of carbon dioxide, what products may remain behind, and how may they be quantitatively determined?

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[1] Bureau of Standards Scientific Paper No. 92, "The Testing of Glass Volumetric Apparatus", by Osborne and Veazey (1908).

[2] Bureau of Standards Scientific Paper No. 182, "Standardization of Potassium Permanganate Solutions by Sodium Oxalate", by R. S. McBride (1912).

[3] Guye: J. Am. Chem. Soc., **30**, 155 (1908).

TABLE II

The Analysis of Known Amounts of NO_2, NO, N_2O, and N_2.

(All the figures given are in milligrams)

No.	NO_2			NO			N_2O			N_2			Total Nitrogen.		
	Taken	Found	Diff.	Taken	Found	Diff.	Taken	Found	Diff.	Taken	Found	Diff.	Taken	Found	Diff.
1	274.8	275.4	+0.6	0.0	1.0	+1.0	—	—	—	—	—	—	83.7	84.3	+0.6
2	—	—	—	—	—	—	86.4	86.0	−0.4	0.0	0.	0.	55.0	54.7	−0.3
3	—	—	—	—	—	—	0.0	0.	0.	39.4	38.6	−0.8	39.4	38.6	−0.8
4	—	—	—	—	—	—	0.0	0.	0.	15.8	16.0	+0.2	15.8	16.0	+0.2
5	464.7	462.4	−2.3	114.5	113.5	−1.0	—	—	—	—	—	—	195.0	193.8	−1.2
6	540.3	535.6	−4.7	68.8	69.1	+0.3	15.0	15.2	+0.2	46.0	46.2	+0.2	252.1	251.2	−0.9

NOTES: 1. The "Total Nitrogen" represents the sum of the nitrogen present in the different gases.
2. Blanks in the table indicate that analyses were not made.

It is reasonably certain that no analyses need be made for nitrohydroxylamic acid, for hyponitrous acid, or for nitramide, because these substances are unstable and, while they might be formed in extremely low concentrations as transitional products, they would hardly be present in detectable amounts at the end of the reaction.

Nitrous acid is somewhat unstable:

$$3HNO_2 \rightleftarrows 2NO+HNO_3+H_2O.$$

and its rate of elimination from solution depends largely on physical factors[1]. The amount of nitrous acid present after passing carbon dioxide through a solution for three hours, depends mainly on the temperature. Qualitative experiments in this laboratory showed that considerable HNO_2 remained after bubbling gas through a solution at room temperature for a long time, and therefore an analysis must be made for nitrous acid in the residual solution from a reduction experiment in which nitric oxide is found as one of the reduction products, unless the solution has been heated to nearly 100°C. for an hour or so, while a moderately rapid stream of inert gas is being passed through. Only under these latter conditions is nitrous acid positively eliminated.

Nitrous acid is a reactive substance, which may act either as an oxidizing or a reducing agent. Hydroxylamine and hydrazine are rapidly decomposed by HNO_2 solutions. For hydroxylamine the reaction takes place mainly with the elimination of N_2O:[2]

$$NH_2OH+HNO_2=H_2N_2O_2+H_2O \text{ and } H_2N_2O_2=N_2O+H_2O.$$

With hydrazine in acid solution, the nitrous acid may form N_2, N_2O, HN_3, or NH_3.[3] Therefore, when nitrous acid is one of the chief reduction products of the nitric acid solution under a definite set of conditions, hydroxylamine or hydrazine will not be present in the solution in appreciable amounts.

When reduction is carried out by "ous" metallic salts, and the reaction takes place rather slowly so that the solution contains both nitric acid and unoxidized salt, it is not probable that much HNO_2 will be present, because of the relative instability of nitrous acid as compared to nitric acid, and the consequent more rapid reduction of the nitrous acid by the "ous" salt.

It is therefore apparent that analytical methods should be given for solutions of free nitric acid containing ammonium salts, strongly-reducing metal salts, and nitrous acid or salts of hydroxylamine and hydrazine[4].

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[1] Knox and Reid: J. Soc. Chem. Ind.,38, 105 (1919).

[2] Meyer: Ann., 175, 141 (1875); Wislicenus: Ber., 26, 771 (1893); Tanatar: J. Russ. Chem. Soc., 25, 342 (1893); Ber., 27, 187 (1894); Ray and Ganguli: J. Chem. Soc., 91, 1866 (1907).

[3] See Browne and Overman: J. Am. Chem. Soc., 38, 298 (1916).

[4] Hydronitric acid is not considered in this discussion except to determine its effect on certain of the analyses for other compounds. It is probable that hydronitric acid would be obtained through the intermediate formation of hydrazine, and hydrazine has not as yet to my knowledge been found among the reduction products of free nitric acid, so this does not seem to be a serious omission. Furthermore HN_3 does not influence appreciably the accuracy of any of the analytical methods to be described, and therefore if complete analyses are made for everything else except HN_3, and still the total recovery falls considerably short of 100% of the reducing agent used, an indication of the presence of hydronitric acid will be obtained which then can be investigated.

In choosing methods for the analysis of these solutions, only those have been considered which can be carried out in an acid solution directly, or which depend on the destruction of the active materials the moment the solution is made alkaline. This should be the case, because in a basic solution new reactions may occur, even though the reagents be considerably diluted, producing new products and destroying the accuracy of the methods.

1. *The Determination of Ammonium Salts.*

This is carried out practically by the method of Suler[1]. Copper sulfate solution is added to the diluted sample in about 100% excess of the amount which will be necessary to destroy the hydroxylamine, hydrazine, and reducing metal salts (using $SnCl_2$ as an example) when the solution is made alkaline. The simplified reactions will be:

$$2NH_2OH+4CuO=2Cu_2O+N_2O+3H_2O$$
$$N_2H_4+4CuO=2Cu_2O+N_2+2H_2O$$
$$SnO+4CuO=2Cu_2O+SnO_2$$

An excess of strong sodium hydroxide solution is then added and the liberated ammonia is steam-distilled into N/10 acid, according to a regular Kjeldahl procedure. After about 50–100 cc. of distillate have been collected, sufficient sodium sulfide solution to completely precipitate as sulfide all the copper and other heavy metals present is added through a separatory funnel in the stopper of the flask containing the alkaline liquid. About 100 cc. more is then distilled over before titrating the excess standard acid with N/10 sodium hydroxide and methyl red indicator. The addition of Na_2S was found to be a necessary modification of Suler's directions in order to make the method accurate in the presence of certain heavy metal salts, notably those of tin. Without it, ammonia tends to be held back in these cases, and the results are low. The sulfide must not be added with the caustic solution, because the destruction of hydroxylamine does not take place then according to the reaction given above, but some of it goes to ammonia. A blank is run to determine the ammonia in the reagents, which is deducted in order to obtain the correct amount of ammonia in the sample.

A few experimental results are given in Table VI, page 530, together with results for hydroxylamine. The distillation results in experiments 10a, 10b, 11a, and 11b, made for hydroxylamine and given in Table V, page 500, show the effect of adding sodium sulfide solution. Experiment 12, Table V, shows that the Na_2S must not be added with the caustic soda.

2. *The Determination of Salts of Hydroxylamine.*

Considerable work was necessary before a satisfactory method for this determination was found. It was originally thought that the answer consisted in finding an oxidizing agent stronger than nitric acid (so as not to reduce nitric acid) which would quantitatively oxidize salts of hydroxylamine to a definite product (either N_2O or HNO_3) in acid solution, without attacking

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[1] Suler: Z. Elektrochemie, 7, 839 (1901).

ammonium salts. However, such a reagent could not be found. Permanganate and dichromate oxidize it to more than one product, and the reactions are neither definite nor quantitative[1]. Neither $HClO_3$, HIO_3, nor H_2O_2 in dilute acid solutions, act with sufficient speed to be of value. Oxidation to nitric acid using a potassium bromate-bromide solution or hypobromite solution[2] requires careful regulation of the acidity of the solution in order to get the reaction approximately completed in the specified time: attempts to use buffers, such as sodium bicarbonate or acid phosphate, for solutions containing varying amounts of strong acids, were unsuccessful. Heating the solution under pressure completes the reaction, but also partially oxidizes ammonium salts. Out of thirty quantitative experiments made with known amounts of hydroxylamine, under conditions similar to those met with nitric acid solutions, and allowed to stand with the oxidizing solution for varying lengths of time up to 16 hours, not one gave more than 99% of the hydroxylamine taken, and most of them were irregular and 3-4% low. It would seem that the primary reaction is rather a slow one, and that side reactions are likely to occur.

In the *complete* absence of ammonium salts, quantitative results were obtained by oxidation to nitric acid using a solution of sodium hypochlorite, through a considerable range of varying acidity. This method consists in placing a measured volume (about 25-50% excess) of slightly alkaline NaClO solution in an iodine flask (ground glass stopper and funnel top) diluting to about 100 cc. and then adding the hydroxylamine salt solution, which must contain more than enough acid to eventually neutralize the hypochlorite, from a pipette with the tip below the surface of the liquid. The acid solution separates out as a second layer below the hypochlorite, and no chlorine is lost. The flask is stoppered and swirled, and after five minutes is cooled under tap water, an excess potassium iodide solution is sucked in around the stopper without allowing chlorine to escape, the flask is shaken, and the liberated iodine titrated at once with standard thiosulfate. A blank determination gives the strength of the hypochlorite, and the chlorine consumed in oxidizing the hydroxylamine (and also the strongly-reducing metal salts, if present) is calculated by difference.

However, the presence of ammonium salts interferes with this method. The ammonium ion either prevents the quantitative oxidation of hydroxylamine in cold solutions, or is itself partially oxidized if the solution is heated. Table III gives some of the experimental results obtained, and shows the bad effect of ammonium salts. The hydroxylamine solution was made from specially purified, ammonium-free hydroxylamine hydrochloride. The hypochlorite

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[1] Knorre and Arndt: Ber., **33**, 30 (1900); Raschig: Ann., **241**, 168 (1887); Z. angew. Chem., **17**, 1411 (1904); Simon: Compt. rend., **140**, 659 (1905). Extensive experiments in this laboratory failed to show any conditions under which these reactions would go to one quantitative end product.

[2] Rupp and Maeder: Arch. Pharm., **251**, 295 (1913); through Chem. Abs., **7**, 3727 (1913).

TABLE III

The Determination of Hydroxylamine Salts by means of Hypochlorite Solution.

No.	NH_2OH (Mg)			Grams Present				Time of Standing	Temperature °C.
	Taken	Found	Diff.	$(NH_4)_2SO_4$	HNO_3	HCl	H_2SO_4		
1	10.10	10.11	+0.01	—	—	—	4.3	none	20
2	10.10	10.11	+0.01	—	—	—	4.3	10 min.	20
3	5.05	5.03	−0.02	—	—	—	2.2	10 min.	20
4	25.25	25.35	+0.10	—	—	—	10.8	none	20
5	10.10	9.91	−0.19	—	—	2.4	20.3	none	20
6	10.10	10.10	0.00	—	—	2.4	20.3	5 min	20
7	10.10	10.17	+0.07	—	—	—	4.3	5 min	20
8	10.10	9.46	−0.64	1.	3.3	2.4	20.3	5 min.	20
9	10.10	9.66	−0.44	1.	3.3	—	4.3	5 min.	20
10	10.10	10.18	+0.08	—	3.3	—	4.3	5 min.	20
11	10.10	9.10	−1.00	0.05	—	—	4.3	12 hours	20
12	10.10	9.45	−0.65	0.05	—	—	8.6	12 hours	20
13	none	0.00	0.00	—	2.5	—	—	30 min.	95
14	none	21.	+21.	1.	—	2.4	—	30 min.	95
15	none	20.	+20.	1.	2.5	—	—	30 min.	95

method was finally abandoned as a general method for this work because of its failure in the presence of ammonium salts.

The true amounts of hydroxylamine salts present in the pure solutions taken, were determined by the ferric salt method, which has been shown to be correct when properly carried out[1]. Some of the first attempts in this laboratory to use this method produced discordant results. Investigation of the cause emphasized how sensitive the method is to changes in the dilution and in the amounts of ferric sulfate and acid present. Results of titrations for a solution made by dissolving pure hydroxylamine hydrochloride in 1:3 sulfuric acid, are given in Table IV. The last two results in this table represent entirely satisfactory determinations. Experiments numbered 1 to 6 failed mainly because the acid concentration was too high. In experiments 7 and 8 the acid concentration was all right, and the *amount* of ferric sulfate would have been all right if the total volume of the solution had been smaller, but the volume of the solution was sufficiently large to reduce the concentration of the ferric sulfate to a value which did not give complete reaction, even with twenty minutes of boiling. The influence of concentration of both sulfuric acid and ferric sulfate is thus illustrated.

The directions for this determination given in Treadwell-Hall[2] call for the equivalent of 3.5 gm. of sulfuric acid, and 5.0 gm. of $Fe_2(SO_4)_3$, but do not specify the final volume of the solution. If it be assumed that application of the directions would usually result in about 70 cc, of solution, then the concentration would be about 5 gm. of H_2SO_4 and 7 gm. of $Fe_2(SO_4)_3$ per 100 cc. Bray and his collaborators used a solution containing 8.8 gm. of acid and 1.42 gm. of ferric sulfate in 90 cc.; or 9.8 gm. H_2SO_4 and 1.58 gm. $Fe_2(SO_4)_3$ per 100 cc. It would appear that the excess of ferric sulfate advocated by Treadwell-Hall is unnecessarily large.

Consideration of these facts suggests that the following directions be used for carrying out the determination of hydroxylamine by the ferric salt method:

To a solution (in a 500 cc. Erlenmeyer flask) containing the equivalent of about 0.05 gm. of NH_2OH, add dilute sulfuric acid, and then ferric sulfate solution, or ferric alum solution, until at least 2 gms. of $Fe_2(SO_4)_3$ are present and the concentration of the final mixture corresponds to 8 grams of H_2SO_4 and 3 grams of $Fe_2(SO_4)_3$ per 100 cc. of solution. Heat to boiling and boil vigorously for 5 to 10 minutes. Cool, dilute to about 200 to 300 cc. and titrate with N/10 permanganate solution. Run a blank on the reagents and subtract this from the value found in order to get the volume of the permanganate equivalent to the hydroxylamine.

The method which was finally developed for the quantitative determination of hydroxylamine salts in nitric acid solutions containing ammonium salts, is based on the reduction of hydroxylamine salts to ammonium salts by

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[1] Bray, Simpson and MacKenzie: J. Am. Chem. Soc., 41, 1363 (1919). Obviously this method cannot be used in the presence of nitric acid, because hot nitric acid solutions oxidize ferrous sulfate.

[2] Treadwell-Hall: "Analytical Chemistry", Vol. II, 631 (1915).

TABLE IV

The Determination of Hydroxylamine Salts by the Ferric Salt Method.
(All experiments were made with 25.00 cc. samples of one hydroxylamine solution.)

No.	Composition of Solution			Per 100 cc. of Solution.		Boiling Time	Volume of std. $KMnO_4$ req. in Titration	Character of End. Point
	H_2SO_4 Gm.	$Fe_2(SO_4)_3$ Gm.	Total Volume Cc.	H_2SO_4 Gm.	$Fe_2(SO_4)_3$ Gm.	Min.	Cc.	
1	30.3	2.08[1]	105(+)	29.0(−)	1.98(−)	5(+)	28.17	—
2	30.3	2.08[1]	105(+)	29.0(−)	1.98(−)	5(+)	30.20	Bad
3	30.3	2.08[1]	105(+)	29.0(−)	1.98(−)	5(+)	26.40	—
4	30.3	2.08[1]	105(+)	29.0(−)	1.98(−)	5(+)	26.22	—
5	30.3	1.50	100	30.3	1.50	5	30.+	Bad
6	39.1	3.00	150	26.0	2.00	5	27.1	—
7	30.3	1.50	350	8.7	0.43	5	31.+	Bad
8	30.3	1.50	350	8.7	0.43	20	27.00	Fair
9	21.5	5.2[1]	225	9.6	2.31	5	26.10	Sharp
10	21.5	5.2[1]	225	9.6	2.31	20	26.10	Sharp

[1] Ferric sulfate added in the form of ammonium-iron alum.

NOTE: In the first four experiments, the amounts of H_2SO_4 and $Fe_2(SO_4)_3$ taken were as given, but the importance of the concentration of the solution was not realized, and small variable amounts of wash water were added. This is indicated by (+) for the total volume of the solution, and (−) for the other constituents. The boiling time ran over five minutes in some of these cases.

means of a titanous salt in acid solution. Titanous salts were first used in quantitative work by Knecht and Hibbert[1]; Stähler[2] showed that they would reduce hydroxylamine to ammonium salts, which could then be determined by distillation; and Bray[3] and his collaborators have shown recently that titration of hydroxylamine salts with standard titanous salt solution gives quantitative results.

The present work consisted in finding the conditions under which hydroxylamine salts could be quantitatively reduced to ammonium salts, without reducing nitric acid appreciably. When first attempted, this seemed almost impossible, but it was found that when the reduction is carried out in a solution heavily buffered with mono-sodium di-acid phosphate, and therefore containing H_3PO_4 as the chief free acid, the reduction of nitric acid takes place at such a low relative velocity that the results correspond to quantitative reduction of the hydroxylamine to ammonium salts, which can then be determined by distillation. If the concentration of the nitric acid is relatively too high, nitrous acid will be formed by its reduction, and that portion of the hydroxylamine which has not yet been reduced to ammonia will be partially oxidized by the nitrous acid and destroyed as nitrous oxide, causing less ammonia formation and low results. Nitric acid never seems to be reduced to ammonium salts at all under the conditions of this determination. The excess titanous salt is destroyed by the addition of copper sulfate solution, before adding the caustic soda and distilling out the ammonia.

A few of the experiments by which this method was developed are given in Table V. Experiments 1 and 2 show that nitric acid is not reduced to ammonia by the titanous salt. Experiment 3 gives an extremely low result because dilute nitric acid alone is rapidly reduced to HNO_2 (mainly) by $TiCl_3$ and this destroys the hydroxylamine before it can be reduced to ammonia. Experiment 4 shows the beneficial effect of sulfuric acid, and experiments 5 and 6 indicate that almost quantitative results are obtained in a solution containing free sulfuric acid and heavily buffered with sodium sulfate. Experiments 7, 8 and 9 show that H_3PO_4 and NaH_2PO_4 are effective for retarding the rate of reduction of the nitric acid to a point which permits quantitative reduction of NH_2OH to NH_3, and 9 shows that the presence of a little copper ion does not affect the result. Experiments 10a, 10b, 11a, and 11b show the necessity for using sodium sulfid in the presence of tin salts, and experiment 12 proves that the Na_2S should not be introduced with the caustic soda.

The recommended method consists in adding a measured volume of the sample to a solution containing NaH_2PO_4 in excess of the amount equivalent to the acid present, according to the reaction:

$$NaH_2PO_4 + H(Acid) \rightleftarrows Na(Acid) + H_3PO_4.$$

In practice, 100 cc. of phosphate solution (containing approximately 200 grams of $NaH_2PO_4 \cdot H_2O$ and 10 cc. of syrupy phosphoric acid per liter) is placed in a

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[1] Knecht and Hibbert: Ber., 36, 166, 1549 (1903); 38, 3318 (1905).

[2] Stähler: Ber., 42, 2695 (1909).

[3] Bray, Simpson and MacKenzie: Loc. cit.

TABLE V

Experiments developing the Titanous Salt Method for the Determination of Hydroxylamine in the Presence of Nitric Acid.

No.	NH₂OH Taken Mg.	NH₂OH Found Mg.	NH₂OH Error %	Other Substances Originally Present: HNO_3 Gm.	H_2SO_4 Gm.	HCl Gm.	$SnCl_2$ Gm.	H_3PO_4 Gm.	NaH_2PO_4 Gm.	Na_2SO_4 Gm.	$CuSO_4$ Gm.	Na_2S Soln. Used Cc.	Total Volume Cc.
1	0.0	0.0	0.0	1.6	10.7	—	—	—	—	—	—	—	306
2	0.0	0.0	0.0	1.6	—	—	—	—	20	—	—	—	260
3	44.6	21.7	−51.	3.3	—	—	—	—	—	—	—	—	316
4	44.6	40.0	−10.3	1.6	10.7	—	—	—	—	—	—	—	306
5	44.6	44.8	+0.5	—	10.7	—	—	—	—	20	—	—	285
6	44.6	44.0	−1.4	1.6	10.7	—	—	—	—	20	—	—	285
7	44.6	44.5	−0.1	1.6	—	—	—	11.8	—	—	—	—	306
8	44.6	44.9	+0.7	4.9	—	—	—	—	20	—	—	—	270
9	44.6	44.4	−0.6	1.6	—	—	—	—	20	—	0.4	—	270
10a	44.6	42.9[1]	−3.8[1]	—	—	0.3	0.6	—	10	—	—	—	155
10b	44.6	45.0[1]	+0.9[1]	—	—	0.3	0.6	—	10	—	—	10	155
11a	44.6	42.0[1]	−5.8[1]	—	—	0.3	0.6	—	10	—	—	—	155
11b	44.6	45.4[1]	+1.8[1]	—	—	0.3	0.6	—	10	—	—	10	155
12	(44.6)[2]	3.0[2]	large[2]	—	—	—	—	—	—	—	—	10	110

[1] Experiments 10a and 11a were made complete. Then Na_2S was added to the flask and more distillate was collected. This was titrated, and the result added to that for 10a and 11a, and called 10b and 11b.

[2] This solution was not reduced with $TiCl_3$. The $CuSO_4$ was added and then a mixture of Na_2S and NaOH.

1-liter Florence flask and a measured volume of the sample is mixed with it. A 20 per cent $TiCl_3$ solution, free from ammonia, is added in small portions with swirling until the solution is colored purple. Then about 2 cc. more is added in excess, the flask is covered and allowed to stand at room temperature for an hour, this amount of time being required because the last portions of the hydroxylamine are rather slowly reduced under these conditions. A white precipitate is produced by the oxidized titanium. To the solution, which should still be purple denoting an excess of titanous salt, is added copper sulfate solution in excess of the amount necessary to oxidize the "ous" salts present, and the rest of the analysis is completed as described above for the determination of ammonia, sufficient sulfide being added in the middle of the distillation to precipitate the titanium as well as the copper and any other heavy metals which may be present.

This method, when corrected for the ammonia in the reagents, gives the sum of the ammonia originally present, and that produced by the reduction of the hydroxylamine. The hydroxylamine is calculated by difference between this determination and that of the ammonia only.

Results of experiments with known solutions are given in Table VI. Experiments 12 and 13 indicate that the results obtained for NH_2OH in the presence of hydrazine or hydronitric acid are only very slightly high, showing that the method is still applicable in the presence of these substances.

3. *The Determination of Salts of Hydrazine.*

It is a rather remarkable fact that hydrazine, which is a strong reducing agent, should be rather stable in moderately dilute nitric acid solutions. However, quantitative experiments in this laboratory showed that a solution of 30% nitric acid containing a little hydrazine may be heated to 90°C. and then cooled again at once with an almost negligible loss of N_2H_4. Another such solution heated in a bath of boiling water for an hour showed 50% of the hydrazine remaining unchanged, the rest having gone partly to hydronitric acid and probably also partly to ammonium salts and other products. Sabanejeff[1] has made two stable nitrates of hydrazine, $N_2H_4 \cdot HNO_3$ and $N_2H_4 \cdot 2HNO_3$, the first of which he heated to 300° with some volatilization, without decomposition; but when he heated it in a free flame it exploded.

Thus it is apparent that if hydrazine is once formed in moderately dilute, cold nitric acid solutions, it is not likely to undergo decomposition unless nitrous acid is present, in which case it will be destroyed with the formation of N_2, N_2O, HN_3 or NH_3.

Rimini[2] has shown that potassium iodate solution quantitatively oxidizes hydrazine to nitrogen. Jamieson[3] has applied to this reaction the general analytical method developed by Andrews[4] for titration with standard iodate solutions, and has shown that it is accurate. This method is simple and rapid,

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[1] Sabanejeff: Z. anorg. Chem., 20, 24 (1899).

[2] Rimini: Gazz. chim. ital., 29, 265 (1899).

[3] Jamieson: Am. J. Sci., (4) 33, 352 (1912).

[4] Andrews: J. Am. Chem. Soc., 25, 756 (1903).

TABLE VI

The Analysis of Solutions containing Nitric Acid and Salts of Hydroxlyamine and Ammonia.

No.	NH_3			NH_2OH			Used			Other Substances Present		Total Vol. Soln. Cc.
	Taken Mg.	Found Mg.	Error %	Taken Mg.	Found Mg.	Error %	H_3PO_4 Gm.	NaH_2PO_4 Gm.	$TiCl_3$ Soln. Cc.	Gm.	Gm.	
1	0.0	0.0	0.0	44.6	—	—	—	—	—			110
2	17.0	17.0	0.0	—	—	—	—	—	—	0.6 $SnCl_2$		120
3	17.0	17.0	0.0	44.6	44.7	+0.2	—	18	3	0.6 $SnCl_2$	1.6 HNO_3	210
4	—	—	—	63.6	63.1	−0.8	—	10	5	0.8 H_2SO_4		200
5	—	—	—	63.6	63.2	−0.6	—	10	5	2.0 H_2SO_4		200
6	—	—	—	126.2	125.2	−0.8	0.7	10	8			210
7	—	—	—	126.2	125.8	−0.3	1.4	20	8	2.5 HNO_3		210
8	—	—	—	132.6	131.3	−0.8	0.7	10	8	2.5 HNO_3		210
9	—	—	—	132.6	130.9	−1.1	0.7	10	8	2.5 HNO_3		210
10	—	—	—	44.6	44.8	+0.5	1.4	20	6	4.1 $NaNO_3$		170
11	—	—	—	44.6	44.7	+0.2	15.4	20	6	4.1 $NaNO_3$		180
12	—	—	—	44.6	45.5	+2.0	1.4	20	5	1.6 HNO_3	0.04 N_2H_4	185
13	—	—	—	44.6	45.4	+1.8	1.4	20	5	1.6 HNO_3	0.10 HN_3	170

and experiments were made in this laboratory to determine its applicability to nitric acid solutions containing hydroxylamine and ammonium salts.

The method consists in placing the sample in a 250 cc. glass stoppered bottle, adding water and concentrated hydrochloric acid in the proper ratio, and 6 cc. of chloroform, and titrating with N/10 KIO_3 solution with intermediate stoppering and vigorous shaking, until the pink color which develops in the chloroform layer, is sharply discharged at the end point.

The first reactions which take place are:

$$15N_2H_4+10HCl+10KIO_3=15N_2+30H_2O+10KCl+10HI.$$

and: $10HI+2KIO_3+2HCl=2KCl+6H_2O+6I_2.$

or: $15N_2H_4+12HCl+12KIO_3=15N_2+36H_2O+12KCl+6I_2.$

In concentrated hydrochloric acid solution, a further reaction takes place:

$$6I_2+18HCl+3KIO_3=15ICl+9H_2O+3KCl.$$

The total reaction in strong hydrochloric acid solution is:

$$N_2H_4+KIO_3+2HCl=N_2+ICl+3H_2O+KCl.$$

When the iodine is set free at first, it dissolves in the chloroform layer and colors it pink. As more iodate is slowly added with shaking, the free iodine is oxidized to ICl which dissolves in the aqueous layer and gives it a light yellow color. At the end point all the free iodine is destroyed, and the pink color sharply disappears from the chloroform layer.

A summary of the hydrazine experiments is given in Table VII. When there is more than 50 cc. of conc. HCl (Sp. Gr. 1.20) per 100 cc. of aqueous solution *at the end point*, the reduction of the hydrazine proceeds very slowly, and consequently the end point is bad and the results low unless considerable time is allowed for completion of the reaction before adding the last two or three drops of iodate solution. This is illustrated by experiments 1 and 2. When there is less than 50 cc. but more than 25 cc. of conc. HCl per 100 cc. of aqueous solution, the results are quantitative and the end point sharp. This is shown in experiments 2 and 3. When less than 25 cc. of conc. HCl is present per 100 cc. of aqueous solution, the results are high. The amount of this error increases and the end point becomes less sharp as the amount of hydrochloric acid is decreased. Experiments 5, 6, and 7 illustrate this effect, and it is evidently due to the decreased stability of iodine chloride. In experiments 8 and 9 it is shown that free sulfuric acid exerts a stabilizing effect on both hydrazine and iodine chloride, and therefore a smaller quantity of hydrochloric acid is necessary. Experiments 10 and 11 show that small quantities of nitric acid, hydronitric acid, or ammonium salts do not affect the determination. Experiments 12 to 15 show that hydroxylamine is oxidized by the iodate at a rate which depends on the amount of hydrochloric acid in the solution. With small quantities of HCl, the hydroxylamine is oxidized at such a rapid rate that large errors are introduced in the determination of the hydrazine; but with acidities approximating the equivalent of 50 cc. of conc. HCl per 100 cc. of aqueous solution at the end point, hydrazine may be practically quantitatively titrated in the presence of small amounts of hydroxylamine.

TABLE VII

The Determination of Hydrazine by Iodate Titration in Strong Hydrochloric Acid Solution.

No.	N_2H_4			Other Substances Present.					Conc. HCl Cc.	Total Aq. Vol. at End Point Cc.	Ratio Cc. Conc. HCl per 100 cc. Soln at End Point	Character of End Point
	Taken Mg.	Found Mg.	Error %	NH_2OH Gm.	$(NH_4)_2SO_4$ Gm.	HNO_3 Gm.	H_2SO_4 Gm.	HN_3 Gm.				
1	3.30	3.30[1]	0.0	—	—	—	—	—	20	36	56	See note
2	3.30	3.22	−2.4	—	0.25	—	—	—	25	46	54	Bad
3	3.30	3.30	0.0	—	—	—	—	—	15	36	42	Sharp
4	3.30	3.30	0.0	—	—	—	—	—	10	36	28	Sharp
5	3.30	3.32	+0.6	—	0.25	2.5	—	—	10	46	22	Sharp
6	3.30	3.35	+1.5	—	—	—	—	—	10	66	15	Sharp
7	3.30	3.42	+3.6	—	—	—	—	—	10	116	9	Fair
8	3.30	—	—	—	—	—	10.8	—	10	36	28	No color
9	3.30	3.32	+0.6	—	—	—	10.8	—	10	72	14	Sharp
10	3.30	3.32	+0.6	—	0.25	2.5	—	0.02	10	48	21	Sharp
11	3.30	3.32	+0.6	—	—	—	—	0.10	10	46	22	Sharp
12	8.25	8.	−?	0.01	—	2.5	—	—	30	60	50	Bad
13	3.30	3.28	−0.6	0.01	—	2.5	—	—	40	92	44	Sharp
14	16.50	16.90	+2.4	0.05	0.25	2.5	—	—	45	97	46	Sharp but returned.
15	3.30	4.+	+21.+	0.03	0.25	2.5	—	—	10	47	21	None

[1] In this experiment an approximate end point was obtained at once corresponding to 3.1 mg. of N_2H_4. After standing 30 minutes, the $CHCl_3$ was a bright pink, and this color was very sharply discharged corresponding to a total of 3.30 mg. N_2H_4.

The conclusion drawn from these experiments is that this method for the determination of hydrazine is good. For accurate results the acidity of the aqueous solution should correspond to between 25 and 50 cc. of conc. HCl (Sp. gr. 1.20) per 100 cc. *at the end point*. Under these conditions the method is quantitative in the presence of small amounts of sulfuric, nitric and hydronitric acids, and ammonium salts. The presence of other free mineral acids besides hydrochloric may reduce the limits for HCl. Too much hydrochloric acid diminishes the rate at which the hydrazine is oxidized and may make it impossible to get any pink color at all in the chloroform layer; too little hydrochloric acid produces a returning end point and high results. Hydroxylamine is oxidized by iodate in HCl solutions at a rate which depends on the acidity of the solution. By working at the extreme permissible upper limit of HCl concentration, it is possible to determine hydrazine with practically quantitative accuracy in the presence of small amounts of hydroxylamine, but with lower acidities the results for hydrazine will be too high. No pink color is developed in the chloroform layer if an attempt is made to titrate a sample of dilute nitrous acid. In order to test an unknown sample for hydrazine (or other similar strong reducing agent) it is sometimes convenient to add it to a bottle containing the residue from a previous titration which is at the end point: the reducing agent causes a return of the pink color to the chloroform layer.

4. *The Determination of Nitrous Acid.*

In the general discussion on pages 563 to 564 the conditions under which nitrous acid will remain in solution have been considered in some detail. Analyses for nitrous acid should be made as quickly as possible, as the quantities present are likely to undergo rapid variation. Three possible methods of analysis for nitrous acid are suggested. In all cases care must be exercised in order to be sure that it is really nitrous acid which is being determined.

(a) If unoxidized "ous" salts are present, the nitrous acid will probably occur only in very small quantities which can best be determined by colorimetric methods. A test using meta-phenylenediamine hydrochloride, which develops a yellow color with nitrous acid[1], has been successfully used in this laboratory for nitrous acid in solutions of nitric acid which were being reduced by ferrous sulfate at room temperature. Reduction of nitric acid by ferrous sulfate goes on so slowly in diluted solutions, as to have practically zero velocity, and it is therefore possible to prepare a comparison blank having practically the same concentration of reagents as the diluted sample, but containing no nitrous acid. Known amounts of standard nitrite solution (1 gram of $NaNO_2$ per liter) are added to it. To each tube is added 10 cc. of the color developing reagent (a solution containing 2 grams of meta-phenylenediamine hydrochloride per liter, made slightly acid with sulfuric acid). Small amounts of acid are necessary to cause the color to develop, but since these solutions

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[1] Preusse and Tiemann: Ber., **11**, 627 (1878); Veley: J. Soc. Chem. Ind., **10**, 205, 212 (1891); Phil. Trans. **182**, *A*, 288 (1891).

already contain nitric acid, it is unnecessary to add more. The amount of acid present affects the strength of the color, which is one of the reasons for making the two tubes as nearly alike as possible. The tubes should stand for a half hour at room temperature before being compared. Often a turbidity develops which makes very accurate comparison impossible, and in this case approximate direct dilution and comparison is more satisfactory than using a colorimeter. The test fails in the presence of certain salts, such as those of copper.

The total reducing power of the solution (in the above case this is ferrous sulfate plus nitrous acid) may be determined by a permanganate titration carried out as previously described on page 554 for nitrous nitrogen in concentrated sulfuric acid solutions. In cases where the colorimetric method described for nitrous acid is unsatisfactory, it may be possible to estimate it colorimetrically using Griess reagent[1] (sulfanilic acid and alpha naphthylamine) although no experiments have been made in this connection in this laboratory.

(b) When nitrous acid occurs in considerable quantity, strongly-reducing metal salts, hydroxylamine, and hydrazine are probably absent. The nitrous acid may then be determined by the permanganate titration method as given on page 554 for nitrous nitrogen in concentrated sulfuric acid solutions. The disadvantages of the permanganate titration method are: first, that it fails to distinguish between nitrous acid and other reducing substances and these latter, if nitrogen compounds, will probably not be quantitatively oxidized to nitric acid; and second, that when applied to the residual solutions from a complete analysis with the apparatus shown in the first portion of this paper, it fails to permit account to be taken of small amounts of nitric oxide (continuously being liberated from the nitrous acid solution) which remain in the free gases within the apparatus at the end of the run.

(c) The solution containing nitrous acid may be decomposed by heating to nearly 100°C. while a moderate stream of inert gas is passed through for about an hour, and the nitric oxide which results from this decomposition may be caught in a definite volume of concentrated sulfuric acid containing a little nitric acid, and later titrated as previously described. Since nitrous acid enters into an equilibrium with nitric oxide and nitric acid, there is usually no advantage in distinguishing between nitrous acid and nitric oxide, as reduction products. In order to make it possible to apply this method of analysis together with the complete scheme of analysis for the gaseous products, the by-pass I, shown in Fig. 3, has been placed on the first absorption bottle so that the gases may be run directly from the bottle in which the reaction takes place (which is shown in Fig. 3a, and when in use is substituted for E, F and G in Fig. 3) into the second absorption bottle where the nitric oxide is absorbed. The gases are passed through the absorption train as previously described, for three hours, and then the reaction bottle is heated in a water bath (steam-heated) at 90 to 95°C. for an hour while a moderately rapid stream of carbon dioxide carries the gases directly into the second absorption bottle,

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[1] Lunge and Lwoff: Z. angew. Chem., 7, 348 (1894); Lunge: "Tech. Methods of Chem. Analysis" (Eng. Trans. by Keane), *I* 377 (1908).

beyond which the residual carbon dioxide is vented to the air during this portion of the run. Cold air is blown across the top of the reaction bottle during this heating, in order to cool the gases down to room temperature and prevent them from heating the DeKhotinsky joints or carrying appreciable quantities of water into the sulfuric acid bottle. A plug of glass wool in the exit tube from the reaction bottle, filters out liquid mist.

There is a twofold reason for passing the gases from this decomposition directly into the second absorption bottle. In the first place, in spite of precautions to cool and filter the gases from the reaction bottle, a small amount of nitric acid would be likely to get into the first absorption bottle, and this would introduce an error in the analysis of nitrogen peroxide and nitric oxide. In the second place, a much shorter time is necessary to secure complete transfer of the gases into the absorbing liquid in the second bottle.

This decomposition method for determining nitrous acid is advantageous except in cases for which it is not desirable to heat the nitric acid solution.

5. *The Determination of Strongly-Reducing Metal Salts.*

The analysis for strongly-reducing metal salts in the presence of nitrous acid has been treated in the preceding section of this paper (ferrous sulfate in the presence of nitrous acid, page 574). For determining strongly-reducing metal salts in the presence of hydroxylamine salts, advantage is taken of the fact that hydroxylamine is only a very weak reducing agent in a dilute solution containing free mineral acid at room temperature, and it is thus possible to quantitatively oxidize the strongly-reducing metal salts without appreciably affecting small amounts of hydroxylamine. Choosing stannous chloride as an example of a strongly-reducing metal salt, the acid solution is discharged into a 1-liter Erlenmeyer flask containing a mixture of 700 cc. of water, 25 cc. of 1:1 hydrochloric acid, and a measured volume of standard iodine solution. The excess iodine is titrated *at once* with standard thiosulfate, using starch at the end point. The $SnCl_2$ is calculated from the iodine consumed, according to the reaction:

$$I_2 + SnCl_2 + 2HCl = SnCl_4 + 2HI.$$

When relatively large amounts of hydroxylamine salts are present, small but measurable quantities react with the iodine. For this reason a large dilution is used so as to cut the hydroxylamine concentration down to a minimum. The higher the acidity of the solution, the more stable is the hydroxylamine, and therefore considerable free hydrochloric acid is added. In some cases, it may be an advantage to add even more than is suggested. When a small amount of the hydroxylamine is decomposed, unstable nitrogen compounds (hyponitrous or nitrous acid) are present in sufficient concentration to act as oxygen carriers, and cause a slow return of the end point due to liberation of iodine by oxygen of the air. It is thus quite apparent that the excess iodine should be titrated immediately after adding the sample, and that the first end point reached should be taken as the most correct one. The sample should not be diluted and have the iodine added to it, because some oxidation by dissolved air is likely to take place before the iodine can be added.

TABLE VIII

The Determination of Stannous Salts in the Presence of Salts of Hydroxylamine.
(In each case, 700 cc. of water was taken in a 1-liter Erlenmeyer flask.)

No.	Substances Taken						Standard Thiosulfate Solution.		
	1:1 HCl Cc.	Std. I_2 Soln. Cc.	HNO_3 Gm.	H_2SO_4 Gm.	NH_2OH Gm.	Std. $SnCl_2$ Solution Cc.	Required in Titration Cc.	Equivalent to Sample Cc.	Error Cc.
1a	10	10.00	—	—	—	—	10.58	—	—
1b	10	10.00	—	—	—	—	10.60	—	—
2	10	10.00	—	—	0.24	—	10.00[1]	+0.60[1]	+0.60[1]
3a	10	25.00	—	—	—	10.00	15.30	11.20	—
3b	25	25.00	—	—	—	10.00	15.30	11.20	—
4	10	25.00	—	—	0.24	10.00	14.95	11.55	+0.35
5	10	25.00	5.0	—	0.24	10.00	15.15	11.35	+0.15
6	25	25.00	—	—	0.48	10.00	15.00	11.50	+0.30
7	25	25.00	—	—	0.12	10.00	15.20	11.30	+0.10
8	10	25.00[2]	—	—	—	—	30.68	—	—
9	10	25.00[2]	3.4	10.8	0.02	—	30.68	0.00	0.00

[1] Stood two minutes before being titrated.

[2] A different iodine solution from that used in the first experiments.

The magnitude of the error likely to be encountered when applying this method under different conditions, is shown in Table VIII.

Hydrazine is a somewhat stronger reducing agent than hydroxylamine, and reduces dilute iodine solutions under these conditions more rapidly than hydroxylamine but at a very much slower rate than stannous salts. Should it ever be necessary to make a separation of hydrazine and strongly-reducing metal salts, it is probable that conditions in this titration could be worked out for it, by increasing the acidity, or cooling in an ice bath, or adding starch to the iodine solution before adding the sample. This last suggestion is based on the fact that a few experiments indicated that hydrazine salts in hydrochloric acid solution affected the blue starch-iodide color at a very much slower rate than they did free iodine in solution. In cases where metal salts which act as oxygen carriers, are present, it may be possible to obtain more correct results by working in an atmosphere of carbon dioxide, or other inert gas. The *iodate* titration method might possibly be applied, always keeping the hydrochloric acid concentration considerably above that at which oxidation of hydrazine occurs.

IV. Summary.

Analytical methods have been described for the quantitative determination of reduction products of free nitric acid solutions: namely—nitrogen peroxide, nitric oxide, nitrous oxide, nitrogen, nitrous acid and salts of hydroxylamine, hydrazine and ammonia. A method of analysis has been given for strongly-reducing metal salts in the presence of nitric and other mineral acids, and salts of hydroxylamine and ammonia. Some of these procedures are applications of old methods, others are new. An attempt has been made to give and discuss these methods in as general a way as possible, so as to make it feasible to apply them to a large number of different cases. Applications of modern physical-chemical theory have been made, so as to shed light on previously unrelated results obtained by different experimenters.

A modified spiral gas-washing bottle has been devised, which is particularly adapted for quantitative work. Its advantages are: intimate contact is obtained between the gas and the liquid for a considerable period of time; there are no dead spaces to trap the gas; and the liquid is circulated completely and rapidly.

V. Acknowledgment.

The writer gratefully acknowledges his indebtedness to Professor Wilder D. Bancroft under whoese general direction this investigation was carried out, to Professor A. W. Browne for suggestions in connection with hydrazine and hydronitric acid, and to Mr. C. Herbert Quick and Mr. G. Raymond Gillette, seniors in chemistry, who assisted very capably in certain phases of the laboratory work.

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ON KINETIC SALT EFFECT[1]

BY J. N. BRÖNSTED AND C. E. TEETER, JR.

Primary and Secondary Salt Effect

According to the theory, recently developed by one of the writers[2], the velocity of a bimolecular reaction taking place between the molecules A and B in dilute solution is determined by the expression:

$$v = kc_A c_B \frac{f_A f_B}{f_{AB}} = ka_A a_B \frac{1}{f_{AB}} \qquad (1)$$

where c, a and f indicate concentration, activity and activity coefficient respectively. f_{AB} is the activity coefficient of a complex formed by combination of the two molecules A and B. This expression is of particular use, when ions are involved in the reaction, on account of the very marked changes exhibited by the activity coefficient in dilute solution, these changes being computable, at least approximately from the valence of the ion considered and the total ionic concentration. The change in reaction velocity may be effected, therefore, not only by changing the concentration of the reacting system, but also by addition of neutral salts, as for instance potassium chloride.

On the assumption that in a given dilute salt solution the activity coefficient of a non-electrolyte is approximately unity, and the activity coefficient of ions depends only upon their valence, the following results may be derived: Let A be the molecule of a non-electrolyte, then B and AB will have the same electric charge, and so their activity coefficients will be equal. In this case the fraction:

$$\frac{f_A f_B}{f_{AB}}$$

is unity, and the expression for the reaction velocity becomes:

$$v = kc_A c_B, \qquad (2)$$

i.e. the expression of the classical velocity theory.

If, on the other hand, the complex AB is electrically neutral, i. e., if the molecules A and B are oppositely charged with the same number of charges, then $f_{AB} = 1$ and Equation (1) simplifies into:

$$v = ka_A a_B \qquad (3)$$

which is the velocity expression in the "activity theory" of reaction velocity, which has recently been advanced by several authors[3].

The equations (2) and (3) are thus seen to be special cases of the general equation (1). The classical theory as well as the activity theory are therefore not generally valid, but each of them applicable only to certain groups of chemical reactions.

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[1] From the Physico-chemical Laboratory of the Polytechnic Institute of Copenhagen.

[2] Brönsted: Z. physik. Chem. **102**, 169 (1922).

[3] Harned: J. Am. Chem. Soc. **37**, 2460 (1915); Jones and Lewis: J. Chem Soc. **117**, 1120 (1920); Akerlöf: Z. physik. Chem. **98**, 275 (1921).

For instance, according to this view, the classical theory should be, and actually is, applicable to such a reaction as the inversion of cane-sugar by hydrogen ions, while the activity theory is applicable when the reaction consists for instance in the addition of the ions of hydrogen chloride to a neutral molecule[1].

From the form of Equation (1)—as already shown in the first paper[2]—we learn that addition of salts to a system undergoing a chemical transformation may influence the velocity in two entirely different ways. First the term $f_A f_B / f_{AB}$ may be altered, while the concentrations c_A and c_B remain constant. The effect thus obtained on the velocity is called the *primary kinetic salt effect*, and is what we witness in solutions of strong electrolytes, where the concentration of the reacting ions—on account of the complete dissociation—is invariably given by the stoichiometric composition of the solution. Thus the oxidation of potassium iodide by potassium persulphate, for instance, is strongly accelerated by addition of potassium nitrate on account of a salt effect of this kind.

Second, change in velocity may be due to change in the concentrations c_A or c_B, caused by the addition of neutral salt while $f_A f_B / f_{AB}$ remains unchanged. For instance when catalysing the cane-sugar inversion with acetic acid, addition of sodium chloride has a very marked accelerating effect even at great dilution[3]. This is explained by the dissociation of acetic acid being enhanced by the addition of salts[4]. The kinetic conditions of the process, however, are not influenced by the salt addition, and an effect of this kind upon the velocity is therefore properly termed: *secondary kinetic salt effect.*

The possibility exists of course, and examples might easily be quoted, of primary and secondary salt effects operating simultaneously. The effects may then be additive or they may be opposite and cancel partly or completely. It is not unlikely that the complicated kinetic behavior of concentrated solutions of varying concentration is to a great extent due to the combined influence of the primary and secondary salt effects in connection with the dehydrating influence of the strong salt solutions. The last mentioned influence is probably what we writers in the enhanced catalytic effect of hydrogen ions at moderately high salt concentrations.

Reaction between Chloropentammine and Mercuric Ions

For reactions where the concentrations of the reacting ions c_A and c_B are determined by the stoichiometric composition of the solution, and no secondary salt effect therefore is possible, abundant verification of Equation (1) has already been offered. For the quantitative verification, however, mostly

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[1] Harned and Seltz: J. Am. Chem. Soc. 44, 1475 (1922).

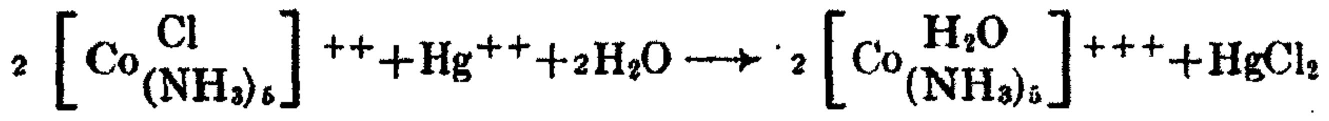
[2] Ref. Brönsted: Z. physik. Chem. 102, 183 (1922). See also Brönsted and Kai Pedersen: Ibid 108, 185 (1924).

[3] Arrhenius: Zeit. physik. Chem. 31, 197 (1899).

[4] Brönsted: J. Chem Soc. 119, 579 (1921).

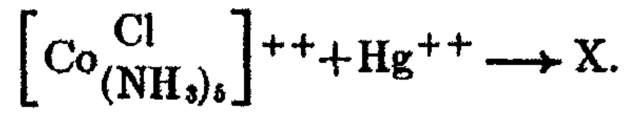
reactions between two negative ions or between ions of opposite sign were considered. It was therefore of interest to try a reaction occurring between two ions possessing both a positive charge.

Such reactions are much less common than reactions involving negative ions. As very fit for our purpose was found the reaction which takes place when mercuric nitrate is added to a solution of chloropentammine cobaltic nitrate. The stoichiometric equation of this reaction is



$$2\left[\mathrm{Co}^{\mathrm{Cl}}_{(\mathrm{NH_3})_5}\right]^{++} + \mathrm{Hg}^{++} + 2\mathrm{H_2O} \longrightarrow 2\left[\mathrm{Co}^{\mathrm{H_2O}}_{(\mathrm{NH_3})_5}\right]^{+++} + \mathrm{HgCl_2}$$

It follows however, the bimolecular scheme, and is therefore kinetically certainly a reaction between one mercuric and one complex cobaltic ion



$$\left[\mathrm{Co}^{\mathrm{Cl}}_{(\mathrm{NH_3})_5}\right]^{++} + \mathrm{Hg}^{++} \longrightarrow \mathrm{X}.$$

Also in the absence of mercuric ions the chloropentammine ion transforms slowly into the aquopentammine or roseo ion[1]. At the concentrations used in our experiments, however, this spontaneous transformation was negligible in comparison with the reaction to be studied.

The chloropentammine or purpureo ion has a red-violet color while the roseo ion is orange-red. The reaction could be followed by the change of color, and the velocity determined from the percentage change.

Solutions of purpureo and roseo nitrates were made up of concentration 0.01 M, and from these 11 standard color solutions according to the following scheme:

Designation	0	1	2	3	4	5	6	7	8	9	10
cc of roseo	0	1	2	3	4	5	6	7	8	9	10
cc of purp.	10	9	8	7	6	5	4	3	2	1	0
cc of water	10	10	10	10	10	10	10	10	10	10	10

These 11 solutions were placed in test tubes of approximately the same diameter and length immersed in a glass thermostat at 20°. A piece of white glass served as background, and daylight as illumination. The color was judged by looking vertically through the column of liquid.

The test solutions, consisting of purpureo nitrate with mercuric nitrate and various amounts of salt, were placed in similar test tubes in a sliding carrier that moved parallel to the file of standard solutions. By carefully judging the colors the degree of transformation could be estimated with an error of 2—4 per cent.

Because of the spontaneous transformation of the purpureo into roseo ion, fresh solutions of the former as well as fresh standard solutions were made up each day. It may be noted that roseo chloride in solution changes to some extent to purpureo salt, and therefore is not very fit for preparing the standard color solutions. Roseo perchlorate is not so transformed and hence may be, and was in part of the experiments, used in place of nitrate.

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[1] Lamb and Marden: J. Am. Chem. Soc. 33, 1873 (1911).

In the following table are given the composition of the solutions expressed as molar concentrations, the total equivalent concentration c and the velocity constant k.

TABLE I

$\left[Co\begin{matrix}Cl\\(NH_3)_5\end{matrix}\right]^{++}$	Hg^{++}	HNO_3	KNO_3	$Sr(NO_3)_2$	c	k
0,005	0,0052	0,005	0	0	0,025	1,76
0,005	0,0052	0,005	0,025	0	0,050	2,46
0,005	0,0052	0,005	0,050	0	0,075	2,95
0,005	0,0052	0,057	0	0	0,077	2,95
0,005	0,0052	0,005	0,100	0	0,125	3,81
0,005	0,0052	0,005	0	0,05	0,125	3,86

The velocity coefficient k was calculated by means of the theoretical expression for a bimolecular process such as the one here considered:

$$\frac{2}{2c_2-c_1}\ln\frac{2c_2-c_1x}{2c_2(1-x)}=kt$$

c_1 and c_2 being the initial concentration of prupureo and mercury ions respectively, x the fraction of the purpureo ions transformed and t the time in minutes. When the readings of transformation in each experiment were plotted against time, curves were obtained which proved in agreement with this expression when the transformation did not exceed 70 per cent.

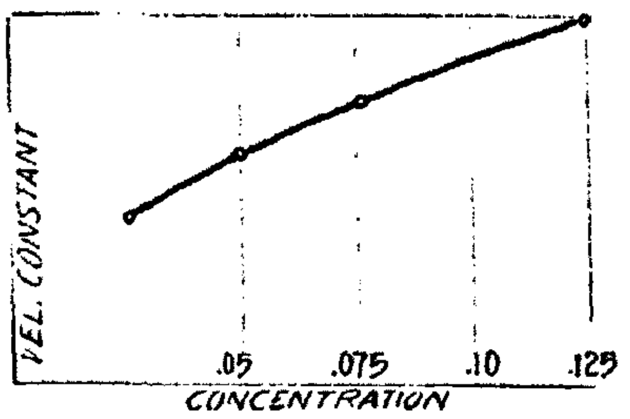

FIG. 1

A glance at the figures in the two last columns and the corresponding diagram, Fig 1, shows the velocity coefficient to increase very markedly with increasing total concentration, as expected from our theory. A calculation of the magnitude of this big salt effect by means of Equation (1) is not possible, because the value of the activity coefficient of tetravalent ions at such concentrations is unknown. The effect seems however to be of a fairly reasonable magnitude.

It is also a characteristic feature of the salt effect here considered, that a change of cation has no or very little influence upon the velocity. K^+, H^+ and $\frac{1}{2}Sr^{++}$ give very nearly the same speed. This fact is in accordance with the principle of the specific interaction of ions[1] since the reacting ions are also cations.

The reaction between the chloropentammine and mercuric ions which is thus seen to conform with our theory of reaction velocity, possesses also in itself much interest. The driving force in the reaction is undoubtedly the strong affinity between mercuric and chlorine ions tending to form the undissociated mercuric chloride molecule. A similar reaction therefore occurs in

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[1] Brönsted: J. Am. Chem. Soc. 44, 877 (1922).

the case of other unstable chlorine compounds. In dichloro-tetramine cobaltic salts the chlorine atoms are not so strongly bound as in the chloropentamine salts, and accordingly the reaction with mercuric ions is much more rapid in this case, as shown by the instantaneous color change, from green to violet, on addition of mercuric nitrate. In the case of the complex bromo compounds the reaction is likewise much quicker, corresponding to their greater instability and the greater affinity between mercuric and bromine ions. The reaction between bromopentammine and mercuric ions for instance, can be traced colorimetrically down to very small concentrations.

While the effect of mercuric ions in all these reactions seems very natural, a similar effect of silver ions to transform complex halogeno ions into aquo ions could by no means be predicted. As a matter of fact, however, silver ions have the same tendency as mercuric ions to accelerate these reactions. The explanation can not be offered simply by the small solubility of the silver chloride, because this salt can not be formed in solid state as a consequence of a collision between the two reacting molecules. The phenomenon seems to indicate, therefore, some kind of complex formation between the silver and halogeno ions. It would be possible to try experimentally the correctness of this view by a general examination of the correlation between reactivity, complex formation and solubility, and examination from which certainly much interesting information could be furnished.

As a substance with a similar effect to mercuric and silver ions may be mentioned undissociated mercuric chloride. The tendency of the $HgCl_2$ -molecule to take up a chlorine ion to form $HgCl_3^-$ is certainly much less than the tendency of the Hg^{++}-ion to a corresponding reaction. Nevertheless its effect is quite definite in several of the reactions mentioned above and the deviations we have found from the scheme of the bimolecular reaction, where the concentration of the mercuric chloride was considerable, may therefore be explained by this effect.

The Decomposition of Diazoacetic Ester by Weak Electrolytes

The important reaction between diazoacetic ester and acids which has been studied by Breding and his coworkers,[1] is to be looked upon as a bimolecular reaction involving the ester molecule and a hydrogen ion. As the first of these is electrically neutral no salt effect is allowed by our theory if the hydrogen ions belong to a strong acid. If, on the other hand, the hydrogen ion belongs to a weak electrolyte we may expect a secondary salt effect. The sign of this effect depends upon the type of the electrolyte.

The process of electrolytic dissociation may give rise to the formation of ions of opposite sign, as in the following instances:

$$EH \longrightarrow E^- + H^+$$

and

$$TH^- \longrightarrow T^{--} + H^+$$

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[1] Fraenkel: Z. physik. Chem. 60, 202 (1907); Spitalsky: Z. anorg. Chem. 54, 278 (1907).

representing the dissociation of acetic acid and the second dissociation step of tartaric acid respectively. In such cases addition of salts in dilute solution always increases the dissociation since in the corresponding equilibrium equations:

$$K_a = \frac{c_{E^-} c_{H^+}}{c_{EH}} f_1^2 \quad ; \quad K_a = \frac{c_{T^{--}} c_{H^+}}{c_{TH^-}} f_2$$

where K_a, the thermodynamic mass action constant is a true constant at constant temperature, and f_1 and f_2 are both decreasing with increasing ion concentration.

On the other hand the electrolytic dissociation may take place with no change in the total number of electric charges as exemplified by the dissociation of the ammonium ion:

$$NH_4^+ \longrightarrow NH_3 + H^+$$

or the hexa-aquo chromic ion:

$$Cr(H_2O)_6^{+++} \longrightarrow Cr\genfrac{}{}{0pt}{}{OH^{++}}{(H_2O)_5} + H^+$$

these processes having essentially the same character of acid dissociations as the dissociation of ordinary electrically neutral acid molecules[2]. The thermodynamic mass-action law gives here:,

$$K_a = \frac{c_{NH_3}\, c_{H^+}}{c_{NH_4^+}}$$

and

$$K_a = \frac{c_2 c_{H^+}}{c_3} \cdot \frac{f_1 f_2}{f_3}$$

c_2 and c_3 indicating the concentration of the bivalent and trivalent chromic ions respectively, and the subscripts of f the valence or charge of the corresponding ion. The dissociation of the ammonium ion accordingly is not, or is very little, affected when neutral salts are added, while in the chromic ion equilibrium the salt addition must cause a decrease in the dissociation, because $f_1 f_2/f_3$ increases with increasing concentration.

We have verified this conclusion of opposite salt effect in the catalytic decomposition of diazoacetic ester by means of acetic acid and hexa-aquo chromic ions, using the pressure of the nitrogen evolved as a measure of the rate of decomposition. The details of the method will be published elsewhere in connection with other measurements.

1. *Acetic acid.* In working out the diazoacetic ester method Fraenkel already used mixtures of acetic acid and sodium acetate as a catalyst, and found the rate of decomposition proportional to the hydrogen ion concentration as calculated by the ordinary mass action law. If, however, the velocity constants thus calculated are plotted against the total ionic concentration of the solution a curve is obtained which shows definitely increasing values of k

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[2] Brönsted: Rec. trav. chim. 42, 718 (1923).

with increasing concentration. From 0.001 N to 0.01N solution the increase is a little more than 6 per cent. This is clearly in agreement with our theory.

In our experiments the salt added to the free acetic acid was potassium nitrate. The first experiments, however, were made with nitric acid in order to test the method, and to determine the catalytic effect of a known concentration of hydrogen ions. In Table II k_1 is the monomolecular velocity constant of each experiment and $k = k_1/c$.

TABLE II

C_{HNO_3}	k_1	k
0.001	0.01347	13.47
0.001	0.01325	13.25
0.001	0.01326	13.26
0.0005	0.00678	13.58
	Average	13.4

The temperature of the experiment was 15°. The mean value in Fraenkel's experiments at the same temperature is k = 13.7.

The following table contains the data for acetic acid of the concentration 0.05 molal with various amounts of potassium nitrate added. For the calculation of k_1 only the first part of the curve was used in order to avoid the complicating influence of the side reaction which takes place in the solutions rich in KNO_3.

TABLE III

Velocity of decomposition of diazoacetic ester catalysed by 0.05M acetic acid in the presence of various amounts of potassium nitrate.

C_{KNO_3}	k_1	$10^4 \times c_{H^+}$	$K_c \times 10^5$
0	0.01268	9.49	1.83
0	0.01266	9.48	1.83
0	0.01271	9.53	1.85
0	0.01281	9.59	1.88
0.005	0.01308	9.72	1.93
0.005	0.01312	9.82	1.96
0.01	0.01351	10.11	2.09
0.01	0.01339	10.02	2.05
0.02	0.01370	10.27	2.15
0.05	0.01419	10.62	2.30
0.10	0.01458	10.90	2.44

From the velocity constant in each experiment the hydrogen ion concentration is calculated by means of:

$$c_{H^+} = \frac{k_1}{13.4}$$

and then the concentration-mass action constant K_c by:

$$K_c = \frac{c^2_{H^+}}{0.05 - c_{H^+}}$$

As expected the dissociation constant thus calculated and given in the last column of Table III *increases* strongly as the concentration of potassium nitrate increases.

2. *Hexa-aquo chromic ion.* In the experiments with the hexa-aquo chromic ion a 0.0105 molal solution of the nitrate was used and various amounts of potassium nitrate added. The results were the following:

TABLE IV

Velocity of decomposition of diazoacetic ester catalysed by 0.0105M. chromic nitrate in the presence of various amounts of potassium nitrate.

C_{KNO_3}	k_1	$10^3 \times c_{H^+}$	$K_c \times 10^4$
0	0.01392	1.04	1.26
0	0.01394	1.04	1.26
0.01	0.01335	1.00	1.16
0.02	0.01290	0.97	1.09
0.05	0.01210	0.90	0.94
0.1	0.01118	0.84	0.82

The dissociation constant K_c is seen, from these figures, to *decrease* with increasing concentration of added salt, contrarily to the behaviour of acetic acid, as expected from the theory.

The total amount of nitrogen evolved in the experiments with 0.1 KNO_3 was only a few per cent less than when no salt was added, which indicates that no side-reaction of significance takes place under the condition of the experiments.

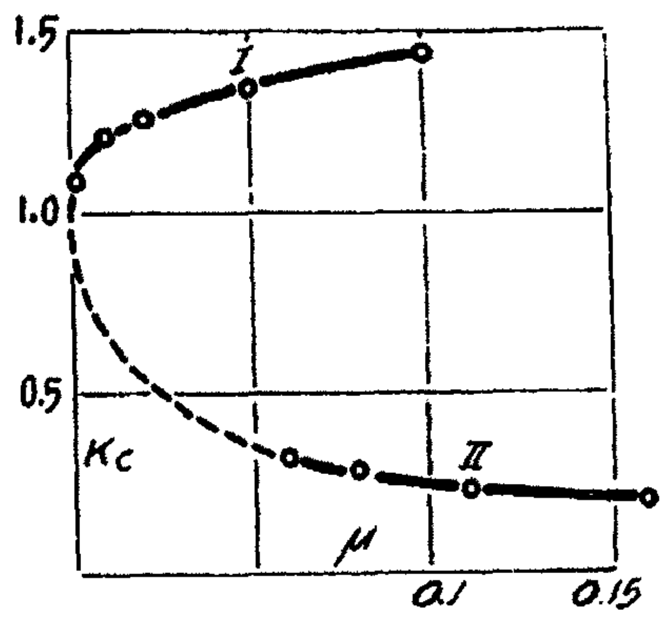

FIG. 2

Comparison of the data with those of Denham[1] and Bjerrum[2] will be made in a later publication in connection with further studies on dissociation and hydrolysis.

The best survey of the salt effect in the two cases considered is obtained by a diagram in which as unity for the dissociation constant K_c is taken its value at infinite dilution, and the relative dissociation constants thus calculated are plotted against the ionic strength[3] as abscissa. The ionic strength μ of a salt is most suitably defined as its equivalent concentration multiplied by the mean value of the valences of its ions:

$$\mu_1 = c_1 \frac{z_1' + z_1''}{2}$$

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[1] Denham: J. Chem. Soc. 93, 53 (1908).

[2] Bjerrum: Z. physik. Chem. 73, 724 (1910).

[3] Lewis and Randall: J. Am. Chem. Soc. 43, 1112 (1921).

and the ionic strength of a solution as the sum of the ionic strengths of each salt present:

$$\mu = \mu_1 + \mu_2 + \cdots$$

Calculation of the dissociation constants at infinite dilution is possible with some approximation from the theory of Debye and Hückel[1] from which the following expression for the activity coefficients is derivable[2]:

$$\log f_z = -0.5\, z^2 \sqrt{\mu}$$

f_z being the activity coefficient of an ion with the valence z.

In Fig. 2 the result of this calculation is presented, the curves I and II giving the change in the dissociation constants of acetic acid and hexa-aquo chromic ion respectively. The dotted parts of the curves correspond to the theoretical calculation. This should give fairly correct results in the case of acetic acid, but is more doubtful in the case of the hexa-aquo chromic ion, because the concentration in the first experimental point down to which the theoretical curve has to be continued is here much higher.

Notwithstanding this uncertainty the diagram conveys a very clear idea of the diversities of the salt effect upon the constants of electrolytic dissociation, according to the type of the weak electrolyte considered.

Summary

1. The "classical theory" and the "activity theory" of reaction velocity in dilute solution are in conformity with a general theory only in special cases, and the velocity expressions of these two theories, therefore, applicable only to certain groups of chemical reactions.

2. The kinetic salt effect may be *primary*, i.e. of purely kinetic origin, only depending upon the activity coefficients, or it may be *secondary*, i.e. caused by a change of the concentration of the reacting ions or molecules, due to a static salt effect.

3. The primary salt effect in the reaction between chloropentammine cobaltic and mercuric ions was experimentally studied and found in agreement with the theory.

4. The secondary salt effect in the catalytic decomposition of diazoacetic ester by acetic acid and hexa-aquo chromic nitrate was experimentally studied and found in agreement with the theory. The effect is positive in the first case and negative in the second case.

Copenhagen, Jan. 1924.

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[1] Debye and Hückel: Physik. Z. 24, 185 (1923).

[2] Brönsted and La Mer: J. Am. Chem. Soc. 46, 555 (1924).

METALLIC LUSTER. I[1]

BY WILDER D. BANCROFT AND R. P. ALLEN

In a previous paper[2] there has been given a discussion of metallic luster chiefly from the view-point of the physicist. In this article it is proposed to take up the subject from the view-point of the psychologist, clearing the way for the next article which will present the subject as the physical chemist sees it.

In 1862 Wundt[3] considered the question of luster in general. "Luster appears most often with specular reflection, because this is the most common way of apparently seeing one object through another. When one looks through a colored glass plate, the objects do not appear lustrous, because one does not see the glass plate as a special object but transfers its color direct to the object looked at. If one lays on a colored glass plate a paper of another color, in which one has cut a small window, and if one holds a little behind the window a white object with a drawing in perspective, the window appears exceedingly lustrous and one can in this way produce monocular, binocular, and stereoscopic luster.

"Luminescence, specular reflection, and luster are to be kept quite distinct. Though luster is often produced by specular reflection, it is entirely different from the latter. An object is self-luminous when it radiates light of the same intensity from the whole of its surface.[4] It is specular reflection when an image of the surrounding objects is obtained which is so good that one forgets the reflecting surface. A substance is lustrous when we see other objects in it but are also conscious of the reflecting surface. The most brilliant luster is therefore produced when vague specular images are obtained and when the surface attracts our attention through its lines, its differences of color, etc. The specular reflections prevent us from seeing the reflecting object clearly and the reflecting object keeps us from seeing the specular reflections well. In nature the dividing lines between luminescence, reflection, and luster are not always sharp, for they depend on us as well as on the objects. Objects which reflect or seem shiny by day usually seem luminous in the dark when one fails to notice slight differences in brightness. A lake with the sun shining on it seems self-luminous when seen from a great distance; it is lustrous when we look at it from a moderate distance; and it reflects when we look down on it from close above. The same object may therefore appear lustrous to one of two observers and reflecting to the other."

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[1] The experiments which led up to this article were made possible by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Bancroft: J. Phys. Chem. 23, 289 (1919).

[3] Pogg. Ann. 116, 627 (1862).

[4] [Wundt is making the tacit assumptions that the temperature is uniform and that we are dealing only with thermal luminescence.]

"We can even see luster with one eye if we make the mirror image of one colored object fall behind the direct image of another colored object. If the colors contrast and if the objects and their boundaries are visible, we get the sensation of brilliant luster. This disappears at once if the reflecting glass plate is turned so that the mirrored image and the one seen directly seem in the same plane, or if the reflected object is so chosen that it covers completely the one seen directly. Everything which helps the judgment as to the distance between the two objects seen one behind the other, increases the intensity of the luster. When the effect of luster is not obtained in the preceding experiment, it can often be produced if one turns the reflected object or the reflecting glass plate a little so that the mirror image changes its position, or if one introduces a perspective drawing on the reflected object. In the latter case an illusion of judgment will sometimes give rise to the sensation of luster even though the planes of the reflected image and of the directly-seen object actually coincide. This luster disappears at once if we use both eyes, because we can then convince ourselves so accurately of the real position of the objects that we are not deceived by the perspective drawing. Conversely—and this actually happens quite frequently—binocular luster may apppear just when the two objects seem to be in the *same* place to monocular vision and become separated only when the convergence due to binocular vision gives us more accurate judgment of the relative positions. Monocular and binocular luster are therefore to be distinguished. Monocular luster will sometimes disappear when one uses both eyes and an object which appears lusterless when looked at with one eye show brilliant luster in binocular vision."

"From these experiments and observations it is clear that the phenomenon of luster is psychological in origin. Luster depends on the impression that we see two or more objects simultaneously, one behind another. The objects seen one behind another differ in color or brightness. So far as sensation goes, it is a blend just as it would be if the objects did coincide in position, in which case the blend would persist in the perception also. This is no longer the case if we consider the objects as at different distances. In this latter case we isolate the color or brightness characteristic of each object from the blended sensation and perceive each separately. When we combine a white and a black object stereoscopically, we do not see a gray or even a lustrous gray; we have the definite impression of seeing the white object through the black one and it is this impression that gives us the sensation of luster. Luster is not a blending but a separation of impressions and it is only because the separation is incomplete that luster interferes with the definite recognition of this fact. *Luster is a process of judgment by which we recognize that the objects seen are at different distances and try to isolate from the blend sensation the color or brightness characteristic of each object.*"

Forty years did not bring much change in Wundt's point of view.[1] "The stereoscopic luster discovered by Dove is a phenomenon which occurs regularly

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[1] Physiologische Psychologie, 4, 625 (1902); 12, 672 (1910).

when we combine stereoscopically two images of different brightness or color, provided we select the conditions so that the effects of contrast, which will be discussed later, do not reach the limit at which a complete displacement of one image occurs.[1] Images with larger expanses of equally-colored surfaces increase the impression of luster while crowded contours tend to destroy the luster because of the contrast effects due to the action of the edges, as will be explained later. On the other hand the fact that one sees the outlines of the object is favorable to the sensation of luster. One gets the best effect therefore when one combines two equally large and definitely bounded surfaces, one of which is white and the other gray, or which are colored differently, provided the differences of intensity are not so great as to cause displacement of one image by the other. Stereoscopic luster is therefore the characteristic phenomenon of binocular blending. A binocular blending of colors or brightness rarely occurs without luster. The essential thing in the production of luster does not consist, as is sometimes assumed, in the greater intensity of the impression; but chiefly in the fact that a surface of a definite color or brightness is seen behind a surface of another color or brightness. Luster, transparency, and reflection are therefore closely connected phenomena which merge one into another. Whenever we see behind one object another which presents fairly distinct outlines and seems therefore at a definite distance behind the other, we get the impression of two surfaces, one nearer than the other, the farther one being seen through the first. The moment the outlines blur a bit, we get the sensation of luster because we have two separate impressions of light but are not able to refer either image to a definite object bounded in any way. From this point of view the peculiar sensation complexes, which characterize the phenomena of transparency, reflection, and luster, are not confined to binocular vision; and stereoscopic luster is a special case in a group of phenomena which occur also in monocular vision. In monocular vision we get the sensation of transparency whenever one eye is acted upon by two lights coming from the same direction but from different distances, provided there is the necessity for accommodation because of limiting outlines for instance. When this is so, we get even under ordinary conditions of vision the impression of transparency which changes to that of luster in the limiting cases. The impression of transparency occurs not only when the object is really transparent; but also in an exactly similar way in case it has a reflecting surface which sends back the image of a second object. This appearance of transparency can easily be produced artificially."

"By means of a glass plate set at an angle, the image of an object *b* on a piece of white paper *c* at one side can be reflected to the eye so as to seem in the same plane or behind another object *a* which is seen directly by looking down through the glass plate. "If the object *a* is very smooth, it can be made to seem like a real mirror. This effect is disturbed if the color of *a* is uneven or if there is a drawing on its surface which forces an accommodation of the eye.

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[1] Dove: Sitzungsber. preuss. Akad. **1850**, 152; **1851**, 246; "Darstellung der Farbenlehre", 166 (1853).

The mirror effect is also disturbed if we give *b* a blurred outline so that it is hard to tell how far behind *a* it seems to be or if we let the white paper *c* be reflected but give it an uneven illumination so that different parts of its reflected image show differences in brightness. In all these cases we get that modification of reflection which we call luster. As a matter of fact, we call a surface reflecting or transparent in case it gives definite reflected images while its own presence is shown in some way, by outline, more brilliant points, or otherwise. On the other hand we call a surface lustrous if the reflected image is not clear in itself or if it cannot be seen clearly because of unevenness in the reflecting surface. Usually both factors are present simultaneously since irregularities in a reflecting surface, which call one's attention to it, usually affect also the clearness of the reflected image. One can therefore produce luster artificially by piling several thin plates, which are both transparent and reflect the light, upon a ground which does not permit light to pass through. The rays reflected from different depths produce a very brilliant luster[1] which, depending on the color of the transparent plates, duplicates in an extraordinary way the luster of metals.

"Stereoscopic luster corresponds exactly to these monocular phenomena of reflection and luster. One can also produce binocular luster with a reflecting glass plate just exactly as in the stereoscope. . . . Reflection and luster are therefore phenomena which are not characteristic of binocular vision as such; but which can evidently be intensified binocularly, as in the duplication of the stereoscopic luster, when the impressions are referred to definitely separated and different objects. Everywhere these phenomena depend on two factors. The first of these is an immediate sensation and is clearly due to the different accommodation made necessary by objects occurring in the same direction from the eyes but at different distances. Since the clear image of any point of the reflecting surface is always surrounded by a diffraction circle due to light coming by the same point from greater distances, the effect of luster will be greater the more diffuse the diffraction circle is, because the characteristic sensation of luster depends on the peculiar combination of clear and unclear vision. The second factor is due to the formation of an impression. The combination of clearly-seen points with diffraction circles gives rise to a certain dissociation of the impressions received on the same point in the retina or on corresponding points in the case of binocular vision. The brightnesses and the colors do not blend completely; but what is seen in the diffraction circles is differentiated more, the greater the qualitative differences. Whenever the actually or apparently reflected object possesses any definite outlines or points, we get the impression of two objects one behind the other, one seen through the transparent other one. This impression gives rise to luster whenever the reflected light is diffuse and clearly marked points or outlines can no longer be recognized."

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[1] Kirschmann: Der Metallglanz und die Parallaxe des indirecten Sehens," Phil. Studien, 11, 147 (1895). I possess a collection prepared by Professor Kirschmann, of combinations of gelatine and mica films which by reflected light can scarcely be distinguished from surfaces of polished gold, brass, steel, copper, silver, and platinum.

Wundt is not distinguishing between metallic and vitreous luster. Many of the cases he is citing are really metallic luster but one gets the sensation of vitreous luster when one has the sensation of depth. As will be shown in the second paper, Kirschmann's layers of gelatine films look like metals because one is not conscious of the light coming from different depths and not, as Wundt puts it, because one is conscious of it. Owing to the failure to differentiate between vitreous and metallic luster, Wundt has been led quite astray, which is perhaps one reason why he never carried the thing any farther.

Ladd and Woodworth[1] say even less than Wundt though in fewer words. "The peculiar perception of lustre is due to a struggle between the two fields of vision which results, not in combining the black images of one field with the white images of the other so as to produce an equal tint of gray, but in a rapid alternation of the two. Very smooth bodies, when they reflect the light perfectly, do not appear lustrous. But when the surfaces of such bodies—as, for example, the surface of a sheet of water—become ruffled by ripples, they become lustrous. The perception of lustre may be produced by combining two stereoscopic pictures of an object which are alike in contour, but one of which is black with white lines where the other is white with black lines. Two such pictures do not combine to produce an equal tint of gray over the whole surface; but the images of the separate points on the two retinas enter into a struggle with each other, and the rapid alternation of the prevalence, first of one and then of the other, gives rise to the appearance of lustre."

The question of metallic luster has been discussed at considerable length by Kirschmann[2] who was a pupil of Wundt's and who is now professor in Leipzig. In the first paper Kirschmann says:

"Dove's well-known experiment, in which two colorless surfaces of different brightness produce the impression of a graphite-like, lustrous surface when combined stereoscopically, proves nothing in regard to metallic luster, although, as a result of this experiment, some authors have identified metallic luster with stereoscopic luster. In the first place it is a false conclusion to consider that the stereoscopic luster in Dove's experiment is metallic luster because it resembles the luster of graphite and the luster of graphite is like the luster of metals. In the second place metallic luster can be seen just as well with one eye as with two. In the only experiment of Dove's, in which monocular luster and in this case metallic luster could be observed, a color on a glass plate appeared red by transmitted light and green by reflected light, and had a luster like copper bronze at certain spots where the two impressions mixed. This latter occurred obviously because the color in question, like indigo and many other glazing colors, had a little metallic luster anyhow and this could be perceived better after painting on glass because of the absence of any disturbing background.

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[1] "Elements of Physiological Psychology", 453 (1911).

[2] Wundt's Philosophische Studien, 11, 147 (1895); Archiv. ges. Psychologie, 41, 90 (1921).

"Aubert, like Brücke and Hering, holds the erroneous view that brightness as such is all-important for luster. Contrast, i.e. great difference in brightness is in his view absolutely necessary, not only for the sensation of binocular, metallic luster but for everything which we call luster. Binocular and metallic luster are here brought absolutely together.

"Wundt has shown, in detail and conclusively, that all luster, binocular and monocular, is due to incomplete reflection or, which is the same thing, to the parallax of the two eyes or to the movement of the single eye; and that marked contrasts, either of intensity or of quality, are very helpful to the appearance of luster. It is difficult to add anything to Wundt's simple and clear exposition on ordinary and stereoscopic luster.

"If the reflection at a plane or a continuously curved surface is approximately completely regular, we have specular reflection. If only diffusely reflected light reaches the eye, we have a matte surface which looks the same from every point of view. In all other cases, in which therefore we have both kinds of reflection (regardless whether real or apparent) in perceptible strength simultaneously, we have the phenomenon of luster.

"We have seen that luster depends upon the simultaneous action of diffusely and specularly reflected light. This can easily lead to the false assumption that our eye has the power of recognizing directly that such light is mixed. We must keep in mind that only a single impression results from the joint action of several, simultaneous light-actions of different quality and intensity on the same part of the retina.

Throughout this article as throughout Wundt's there runs the curious, tacit assumption that metallic luster is the only luster and yet this is contradicted to some extent by the cryptic statement that "it is a false conclusion to consider that the stereoscopic luster in Dove's experiment is metallic luster because it resembles the luster of graphite and the luster of graphite is like the luster of metals." He does not say that stereoscopoc luster either is or is not metallic luster. He merely says that an alleged reason for calling it metallic luster is not a good reason. He is quite clear however that metallic luster is due "to the parallax of the two eyes or to the movement of the single eye." If this were really true, one could not recognize metallic luster with one eye in a thunder-storm at night because many, perhaps most, lightning flashes are over before the eye can move. We found experimentally that the ability to distinguish between a piece of metal and a piece of cardboard was a function both of the time of exposure and of the intensity of illumination. With a given light intensity we could distinguish the sheet tin from the cardboard when the exposure (by means of a photographic shutter) lasted one-fifth of a second; but we could not do so for an exposure of one-tenth of a second. On increasing the intensity of illumination there was no difficulty about telling the tin from the cardboard on exposures of less than one-tenth of a second.

Kirschmann's other definite statement is that luster depends upon the simultaneous action of diffusely and specularly reflected light. "If the reflection at a plane or a continuously curved surface is approximately completely regular, we have specular reflection. If only diffusely reflected light reaches the eye, we have a matte surface which looks the same from every point of view. In all other cases in which therefore we have both kinds of reflection (regardless whether real or apparent) in perceptible strength simultaneously, we have the phenomenon of luster."

There are at least two catches in this paragraph. It may be true that with diffuse reflection from a plane surface we get a matte surface which looks the same from every point of view; but it is not obvious and it has not been proved. The assumption is made tacitly that light can be diffused in only one way and that the surface will look the same from every point of view. That is true only in case the diffusion is absolutely regular which is not a necessary concomitant of diffuse reflection. The second catch is in the clause about both kinds of reflection. So long as Kirschmann says "real or apparent" and sticks to it, he can prove anything. All he has to do is to insist that any case of metallic luster which does not fit in under his formula involves 'apparent' specular reflection and he is safe. We do not see that the superposition of one diffusely reflecting image upon another diffusely reflecting image can be said to give 'apparent' specular reflection and yet, if not, the only escape is to say that stereoscopic luster is not metallic luster and Kirschmann balked in 1895 at saying that definitely, though he implied it. If one limits metallic luster to the luster of metals, the problem is side-stepped and not solved.

In the later paper Kirschmann[1] discusses metallic luster at great length; but the result is depressing, because he apparently knows no physics. "The totally color-blind man sees metallic luster just as well as the color expert. Metallic luster is not affected or weakened in the least by colored illumination even when this is approximately monochromatic, except in so far as this may be due to a decreased intensity of light. In the light of the sodium flame, metallic luster remains unchanged and we must therefore assume that it would not disappear by absolutely monochromatic illumination if such a thing were possible. From this one sees the futility of the earlier attempts to account for metallic luster by the combined action of differently colored components."

It is certainly a gross exaggeration to say that metallic luster is not changed or decreased by monochromatic light when one is dealing with the colors of thin films or with selective reflection from solid dyes, etc. Of course one can say, that these are cases of pseudo-metallic luster and not of true metallic luster; but that will not satisfy anybody. It is very difficult to believe that a totally color-blind man will see metallic luster just as well as the color expert. In so far as metallic luster depends on differing intensities of light, the statement is probably true; but it becomes absurd when the metallic luster depends wholly or in part on differences of color.

"White, the colorless quality of light, is relative. Therefore we recognize a slightly saturated color only when we are reminded continually of its exist-

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[1] Archiv ges. Psychologie, 41, 90 (1921).

ence by the presence of complementary colors. This is the reason why, when we use colored glasses, blue or yellow for instance, we soon forget the monochrome effect over the whole field and think we see things in their natural colors. In the same way we scarcely notice the difference in colors by daylight and artificial light and believe that in lamp light (kerosene, gas, incandescent light) the yellow objects look white whereas really it is the other way round and the white objects look yellow. We do not notice the yellow color because it is over the whole field."

"Colorless surfaces which give complete diffuse reflection and have the same reflection coefficient appear identical; lustrous and especially metallically lustrous ones do not [?]. The total amount of light reflected back from a highly lustrous, dark (black) body may be much greater than that from a slightly lustrous light body. Pure iron is bright white with high luster. Cast iron containing dissolved carbon is also white with less luster. The so-called gray cast iron which contains the coal as small flakes of graphite is much darker and has less luster. Steel, with still less luster, is usually gray."

"The essential characteristic of all luster is a parallactic effect, as has been shown by Wundt and Dove. The surface of a substance is lustrous in all points where a portion of the light is so reflected that it seems to come from points not situated in the surface. The certain recognition of luster therefore presupposes a parallactic process, either a successive or simultaneous observation of different portions of the space, which can be made either with both eyes or by movement either of the eye or of the object. We can define luster as follows: a surface is lustrous when its parts reflect the light in different (adjacent) directions, with different intensity. Or: all portions of a surface are lustrous where one portion of the incident light is reflected regularly and another portion diffusely. Since completely regular reflection is specular reflection, one can look upon luster as imperfect specular reflection."

Here Kirschmann is making the tacit assumption that all cases of metallic luster are due to imperfect specular reflection because some cases are. If he had said that the sensation of metallic luster was due in these cases to suitable differences in intensity, he would not have gone beyond the facts. Misled by his earlier assumption that differences of intensity can only be obtained by a mingling of specular and diffuse reflection, he states his observation in terms of his erroneous hypothesis. He has defined specular reflection as regular reflection from a plane or continuously-curved surface. Under his own definition a metallic surface containing moderately large crystals rising above the surface will not give diffuse reflection because the reflection will be regular from every face and yet there will be differences of intensity and the surface will look metallic. Of course this is not what Kirschmann means by specular reflection; but it is what he seems to say.

"In addition to this actual luster, which we will call true or parallactic luster, there is also an apparent luster dependent chiefly on differences of intensity of adjacent portions of the surface. On account of the specular component of the reflected light, an intense reflection of light is a frequent accompaniment of luster; but this is not necessary or essential. When we note on an object, which we do not consider self-luminous, differences of brightness which our experience would not lead us to expect from diffusely reflecting substances, we often conclude, even when the possibility of parallactic effect is excluded, from analogy with cases where such an effect occurred, that the substance is lustrous. This conclusion may prove to be in error if we are not informed as to the illumination and physical state of the surface; for the actual configuration of apparently brighter and darker portions of the surface may be due to other causes (hidden light-source, transparency, etc.). Only this pseudo-luster can be reproduced by ordinary photography or by the painter, in the latter case only within the ratios of light intensities which the painter's pigments can equal. This latter limitation holds for diapositives whether painted or photographed. No photography and no painting, even though using transparent media and transmitted light, can give the actual parallactic luster by varying light intensities in a plane or continuously-curving surface.

"It is also quite improper, as Katz admits, to recognize luster as a special phenomenon and yet to count self-luminous bodies among the lustrous, as Hering does when he assumes that self-luminous bodies come nearest to those with metallic or silky luster. In certain cases there can be no doubt as to the existence of true, parallactic luster; and the apparent luster can be defined satisfactorily and clearly as an intensity ratio which exceeds the limits of possibility for homogeneous illumination and diffuse reflection. On the other hand our sight organs give us no information whether a surface is self-luminous or is sending reflected light to our eye. We must determine that in some other way, often by making use of other senses. By means of filters we can illuminate a red paper surface with light of the right color, saturation, and brightness, so that it cannot be told in any way from a self-luminous, red-hot metallic surface. Luminosity is not a phenomenon of colors or light qualities but is one of the recognition complexes which we call things. I cannot accept the assumption of Katz that one can see glowing iron as luminous throughout its mass. Glowing iron is absolutely not transparent. When one does not know the objective state of things, one cannot tell it from illuminated objects having the same color, saturation, and brightness."

This is also a bit misleading to the lay reader. Kirschmann seems to say that one cannot be sure whether he is seeing metallic luster or not, until he knows the conditions of illumination; but this is absurd. The essential question is what gives the sensation of metallic luster and it is immaterial whether the sensation of metallic luster is an illusion due to lighting or not. Actually this is not what Kirschmann said. He says that unless we know the conditions we might conclude that the substance is lustrous in itself. That is a perfectly harmless statement; but it has nothing whatsoever to do with the theory of metallic luster.

If we cannot tell whether we are looking at a self-luminous body or not, that would seem to be good and sufficient evidence that the two sensations were the same within the limit of error. It is not justifiable therefore to say that a self-luminous body cannot appear lustrous. When the light falls right on a mother-of-pearl push-button, it is often quite impossible to tell by looking at it whether one is seeing reflected light or transmitted light. It would be foolish to say that the button is lustrous if it is opaque and is illuminated from in front, and is not lustrous if it is translucent and is illuminated from behind, unless we are going to define luster so as to limit it to a sensation produced by reflected light. One could do that; but then one would have to study the nature of the identical sensations which we were calling by different names. Kirschmann's attitude is rather clever if this is simply a contest in dialectics; but it is a distinct failure if one is interested in getting at the truth.

Kirschmann's attitude in regard to the question whether one can see glowing iron as luminous throughout its mass is not satisfactory. He is perfectly right in saying that glowing iron is not transparent. If we look at a mass of molten iron we cannot tell at all how thick it is. On the other hand Katz is right in saying that we get an effect as of luminosity through the mass. The reason for this is that the outer layer of the molten iron is usually cooler than the inner portions and one consequently gets the feeling of depth which means transparency. That is one case. We have another case when the iron or other molten metal is in the furnace and the walls of the furnace are practically as hot as the molten metal. We are then looking into a nearly uniformly lighted space and it is often not easy to detect the surface of the molten metal. To the extent that one is not certain whether one sees the molten metal or the bottom of the furnace, the metal will seem transparent.

"In the previously cited article I have shown that metallic luster must be of a parallactic nature and that it cannot be referred to the co-existence of different degrees of brightness in the same surface, or to intense reflection alone, as some physicists seem to assume. Drude says that it can readily be seen that metallic luster is due only to high reflecting power because an air-bubble looks like a metallically lustrous drop of mercury, whenever the light is totally reflected. There is here the serious confusion of metallic luster, which is properly characterized as incomplete specular reflection, with complete specular reflection. A perfectly polished, and therefore absolutely regularly reflecting, metallic surface has no visible metallic luster at all. We see only the specular reflection of objects and not the mirror surface itself. While traces of diffuse reflection due to dust, small defects, cracks or the like, may be visible, they are usually unimportant in comparison with the specular reflection. Between a well-polished, plane, metallic mirror and the quiet surface of a body of water of sufficient depth, there is no difference in this respect. It would never occur to anybody however to ascribe metallic luster to a reflecting water surface. The air bubble or the test-tube filled with air, gives total reflection in the water and therefore specular reflection but no metallic luster. A surface, which one cannot see and the existence of which one deduces because of seeing mirrored objects, cannot give metallic luster unless one defines metallic luster so as to include all specular reflection. That we can often tell one metallic mirror from another is due to the higher reflecting power of the first, in consequence of which the mirrored images are nearly as intense as the originals. At a completely reflecting surface such as a metallic mirror, one sees no luster of any kind and therefore no metallic luster. That does not exclude the possibility that the light reflected from a metallic mirror may have special properties which cannot be perceived directly [elliptic polarization]. We shall see later that in a metallic mirror the unseen, metallic luster is, in a sense, only sleeping, and can be awakened by suitable means.

"The movement-parallax is a *sine qua non* for all surface luster whether seen by two eyes or by one. This holds also for fatty luster, graphite luster, and for the insufficiently studied lusters of silk and mother-of-pearl. Iridescence and opalescence are also parallactic in nature. In these last cases not only are the intensities, but also the colors of the specularly and diffusely reflected components different. All these sorts of luster can therefore be produced accurately by stereoscopic photography; of course only by transparencies with complete accuracy of the brightness ratios. I have been able to make stereoscopic transparencies of opals which brought out all the characteristics of opalescence to the smallest details.

"Stereoscopy fails absolutely to give metallic luster. When metallically lustrous objects are shown in stereoscopic pictures, there is no luster if they are matte and only the ordinary surface luster when they are polished. And yet I have shown in the previously cited paper by a process of exclusion that metallic luster must be parallactic in nature. Since the binocular parallax plays no part in the recognition of metallic luster and since the latter can be recognized with one eye and when the eye is kept still, the only possible explanation is the parallax of indirect vision. The parallax of indirect vision depends upon the fact that the stationary eye measures the angular distances of points in the field of vision from the fixation point of the line of regard—the center of the cornea image of the pupil—while the moving eye, when measuring angles, takes the center of torsion of the eyeball as its base. The distance between the fixation point of the line of regard and the center of rotation is about 10.5 mm and serves as the base for a triangulation which has no significance at long distances; but which may lead to inaccurate and deceptive values for short distances close to the body and especially within arm's length. In the side portions of the lower field of vision in which we supervise most of the work done by our hands, the parallax of indirect vision must replace the parallax of binocular vision which falls in the relatively slight distance from the fixation point. . . . The difference between the angle of vision and the angle of torsion is the parallax of indirect vision."

Kirschmann states that total reflection cannot give metallic luster because "a surface which one cannot see and the existence of which one deduces because of mirrored objects, cannot give metallic luster unless one defines metallic luster so as to include all specular reflection." It is quite possible to arrange a mercury surface so that one cannot see it and then it will not give metallic luster. On the other hand, one usually can see a drop of mercury on account of the curvature and it certainly looks metallic. In the case of total reflection one does or may see the surface either owing to the curvature or to the irregularities in the glass or elsewhere. Nobody, except a man with a hypothesis to prove, would deny that total reflection may look exactly like mercury. This is quite evident in the following quotation from Brücke.[1] "Pour some water on a table near a window and place a beaker filled with water on the spilled water in such a way that there are air bubbles on the under side of the beaker. If one turns one's face towards the window and looks down at an angle through the water in the glass, the air bubbles look exactly like drops of mercury pressed out flat by the weight of glass. This is much more striking than the better known method of getting metallic luster by dipping an empty test-tube into a cylindrical stand-glass containing water."

Kirschmann states that "it would never occur to anybody to ascribe metallic luster to a reflecting water surface." This may be true if the surface of the water is smooth; but it is not true when the surface is roughened by a slight breeze. Brücke says that "it can be shown that we get the impression of a metallic surface even with substances which have in themselves no metallic luster, provided we have simultaneously a roughened surface and a high reflection of light. The most familiar instance of this is the silvery streak which marks the reflection of the moon from a water surface rippled by the evening breeze. The wavelets make the surface of the water seem rough and the accompanying high reflection of light make the water look metallic, more metallic that the disc of the moon itself."

Following C. du Bois-Reymond, Kirschmann practically postulates that the eye always moves during any exposure however short, a conclusion which is probably not shared by other psychologists.

"Metallic luster, though parallactic in nature, is absolutely independent of the binocular and of the displacement parallax. Every parallax, however, presupposes either simultaneous observation from two different points or movement. Movement of some sort is really at the base of every parallactic determination of depth, even of the simultaneous determination in binocular vision. An absolutely stationary pair of eyes has no way of distinguishing between double images of a single object and single images of correspondingly placed, double objects. It is not the occurrence of double images but their behavior on changing the convergence, which makes us refer them to a single object. In the same way the parallax of indirect vision only becomes conclusive after movement of the eyes and change in the accommodation occur. Metallic luster can be detected on apparently homogeneous surfaces and with an eye which does not move consciously.

"C. du Bois-Reymond has shown however that there is no such thing as an absolutely motionless eye. Even when one seems to be at rest and to be holding one's glance steady, the eye, partly in the socket and partly with the whole head, makes slight vibrating changes in fixation and accommodation which take place involuntarily and unconsciously, but which are large enough

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[1] Sitzungsber. Akad. Wiss. Wien. 43, II, 177 (1861).

to cause the very small displacements in the configuration of the brightness of adjacent points, which are essential in our view to the appearance of metallic luster. . . . All metallic luster presupposes a finite surface. A single point has no metallic luster. It shows only a change in brightness, similar to that of a twinkling star, but without any color appearance. Metallic luster occurs first with the juxtaposition of such small surface units varying more or less in their brightness.

"Katz admits that the appearance of metallically lustrous surfaces differs from those of every other kind of lustrous and diffusely reflecting surfaces; he considers the unusual differences in brightness between the portions of the surface as necessary but not as sufficient. How comes it then that metallic luster can be recognized even with a very slight illumination, when the differences in intensity are no greater than those occurring usually."

"Katz has evidently misunderstood my generalization in the earlier paper that "the form and surrounding of the surface and their relation to other light-impressions in the field of consciousness have no essential effect on metallic luster and that the size of the surface is irrelevant for the occurrence of metallic luster provided the surface is not so small that one gets the impression of a point." He thinks he can use an experiment giving negative results as an argument against my views. By this generalization I have chiefly wished to emphasize that the recognition of metallic luster presupposes a readily perceived surface extension. I have not however assumed that each isolated part of a surface showing metallic luster must of itself show metallic luster. I have nowhere denied that the metallic impression can be made subliminal by special ratios of brightness or contrast, particularly if the amount of surface is small. It is quite obvious that one may see no metallic luster if one shuts off by means of a diaphragm all but a small portion of a surface which as a whole shows metallic luster. In addition Katz has used a 'polished' brass surface and gives no distances. I believe that I have shown that metallic luster involves parallax. Each determination of parallax presupposes a base for the triangulation. The smaller this base, the less the distance at which parallax can be determined. The parallax for indirect vision, which I make responsible for the 'true' metallic luster, has a base of less than one centimeter and consequently metallic luster can be detected only at comparatively short distances. When we think we recognize metallic luster, we are deceived by our 'knowledge of the thing' combined with the recognition of a 'false' luster, for instance, one depending upon unusual differences in brightness, and this luster does not depend upon parallax."

While one cannot agree with all of this, Kirschmann has made a very good point in insisting on the great importance of small areas of uniformity. A checker-board or a spotty effect is much more conducive to the sensation of luster, than when the dark and light portions are separated into two masses.

"How does it happen that at an apparently plane or continuously curved matte or at least incompletely polished metal surface, the conditions arise for an effective parallax of indirect vision, i. e. for a parallactic relation between the components of one and the same narrowly limited sheaf of rays. Here there are only two possibilities: either the metallic surface is not really plane or continuously curved, but proves when examined by sufficient magnification, to consist of many differently oriented reflecting surfaces; or the light sent back by metallically lustrous substances is not reflected at all at the surface; but comes from more or less considerable depths.

"The first of these two assumptions, which seems at first sight the more plausible encounters considerable difficulties when we examine it more carefully. It is impossible to see how the high intensity of metallic reflection is to be reconciled with this assumption, since we must in this case ascribe to metals a practically zero transparency.[1] It must then be an opacity which is not due to absorption. Similarly the sufficiently fine powder of any opaque lustrous grains must show metallic luster.

"The following line of argument tells against this assumption. If one polishes a metal surface, the metallic luster disappears—so far as direct recognition is concerned—in the same measure as the polish approximates perfect reflection. If the reflection is absolutely specular, there can be no metallic luster, as we have previously shown clearly. In the polishing the relative positions of the small metallic particles in the surface are changed considerably. The particles are crushed to some extent and the intermediate spaces become filled with the fragments and with the polishing agent, whereby, naturally, essential changes in the optical properties are brought about.[2] Through polishing there are formed surface films, similar to a thin liquid film, which change considerably the constants calculated from the observations on reflection. If metallic luster were nothing more than very intensive surface luster at a microscopically thousand-fold facetted surface, it must be eliminated by polishing, not only so far as direct observation is concerned, which is the case; but it must be destroyed completely. That, however, does not happen, as we have indicated previously. It is true that with a metallic mirror no metallic luster can be recognized because the completely regular reflection prevents anything being seen except mirror images of objects in front of the mirror. Nevertheless the light thrown back has properties, quite apart from its high intensity, which a non-metallic mirror, such as a water mirror, does not have. One can awaken the slumbering metallic luster by coating the metallic mirror with a thin film of a substance which transmits the light diffusely, such as a matte, shaved or ground, thin sheet of mica, or some other thin film which transmits light diffusely such as a collodion film.[3] The effect is better the thinner the sheet and the finer the grinding. With an ordinary silver-amalgam mirror, one gets the full luster of the silver, the glass film not affecting the phenomenon at all. The same treatment applied to a non-metallic mirror, black glass for instance, gives only a matte surface luster

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[1] There are no absolutely transparent or opaque substances since the amount of light let through is always a function of the thickness.

[2] Drude: Wied. Ann. 36, 532 (1889).

[3] Rayleigh: Phil. Mag. (6) 74, 423 (1917).

something like fatty luster or the luster of graphite. It may be urged that the difference between metallic luster and fatty luster or the luster of graphite is only a difference in intensity; but it is easy to show that this is a false assumption. If one covers a metallic mirror and a black-glass mirror each with a thin film of a medium that transmits light diffusely (mica, gelatine, or collodion,) the differences in the reflecting power make the two surfaces which are now matte of very different brightness. By varying the illumination relatively, it is very easy to bring both to the same degree of brightness; but one then notices that the glass mirror only gives the luster of graphite, while the metallic mirror keeps the luster of matte silver, even though the illumination is very slight.

"If it is, therefore, very difficult to maintain the assumption that an unpolished metal surface behaves like a reflecting surface with a thousand facets, we must then adopt the second of the two suggestions for explaining the parallactic nature of the light reflected from matte metal surfaces, namely that the smallest particles of the metals are completely transparent grains having a very high index of refraction and probably crystalline. These are separated by empty spaces or by an optically much thinner substance. By smallest particles we understand of course the smallest masses which show all the physical-chemical properties of the metal, in extreme cases the physical molecule if there is such a thing, but not the chemical molecule or its constituents, atoms, electrons, sub-electrons, etc. We have nothing to do with the microphysical and physical chemical nature of these particles and we therefore make no assumptions in regard to them. It is also quite irrelevant to our argument what assumptions people make over the transmission of light and especially at the surface of two media. The indisputable part of the wave-theory of light is the periodicity of the process. . . .

"According to our assumption metals are the most transparent of substances, though not necessarily the most permeable to light. The absorption seems to be very slight in them. The light only penetrates a short way because it is soon sent back by total and ordinary reflection at the surfaces of the smallest crystals in consequence of the high index of refraction. In the uppermost layer of crystals of this type, a portion of the incident light is reflected totally as in the case of the diamond. The light which has passed through the first layer, experiences a similar reflection in the second layer, and so on, until, after going through a number of layers, nearly all the light has been emitted in a direction differing by more than 90° from the angle of incidence. Quincke[1] used to believe that light penetrated a measurable distance into metals and was reflected from the inside; but he thought that the depth of penetration was of the order of a wave-length. According to our view this depth is absolutely independent of the wave-length, since the thickness of the layer traversed by the light may be very much less than the actual path of the light, because of the probability of several total reflections sideways. Since the total path is only in exceptional cases an exact multiple of the wave-length,

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[1] Pogg. Ann. **119**, 378 (1863).

there is practically always a difference in phase from which there follows necessarily the elliptical polarization of the light reflected by metals, even when the light is only polarized linearly. Though this thickness may be less than one wave-length, there is a lower limit beyond which no metallic luster is possible. This occurs with very fine precipitates of silver and with gold or iron in fine subdivision. On approaching this limit the metallic luster disappears gradually.

"The light reflected from a metallic surface consists therefore to a small extent of rays actually sent back from the surface, and to a much greater extent of rays which come out from the insides of the transparent metallic crystals after one or more total reflections. If the small metallic particles have a color, which must be faint owing to the high transparency, this must show in the reflected light. The color of gold or of copper is therefore the local [body] color of a transparent substance due to absorption.

"On the other hand we assume that the light, which is transmitted by a thin metallic film, only passes to a very slight extent through the mass of the metal. It has mostly gone through the empty spaces between the metallic crystals and has been reflected from their sides. The color of the light, most of which has only been apparently transmitted and has not actually passed through the insides of the metallic particles, is therefore quite different from the body color of the metal. We therefore have the paradoxical result that the light which is apparently reflected by the metal is really transmitted light, while the light which is apparently transmitted is chiefly reflected light. Since the apparently reflected light will always contain a reflected component, though a very small one,—coming from the outermost surface layer, and since the apparently transmitted light will always contain a small amount of actually transmitted light, the body color of a metal and the color of the light 'transmitted' by a thin film of the same metal will never be completely complementary. The point of view here put forward, that the light has passed through a thin film of metal has been chiefly not in the metal itself, is confirmed by the experimental data on the refraction, and dispersion in such films. According to Kundt[1] and du Bois and Rubens,[2] the eliptically polarized,[3] transmitted light shows anomalous, in fact completely reversed, dispersion, the longer waves in the spectrum having apparently the highest, and the shorter waves the lowest, refrangibility. This effect must however occur if the light has passed through the interstices of a medium having a refractive index higher than unity, provided an uneven number of reflections has occurred. It has been found, however, that gold, silver, and copper are exceptional in that they show normal dispersion. They are therefore classified as metals with normal dispersion.[4] It was found that these three metals have an index of refraction less than unity. It is clear however that here two reversals have compensated

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[1] Sitzungsber. Akad. Wiss. Berlin, **1888**, 255, 1387.

[2] Ibid. **1890** II, 955.

[3] Quincke: Pogg. Ann. **120**, 559 (1863); **129**, 177 (1866).

[4] Rubens: Wied. Ann. **37**, 269 (1889).

each other because a reversed dispersion is normal for substances with indices of refraction less than unity. Of course this low index of refraction is not that of the metal but of the medium in the 'empty' interstices. The analogy between the behavior of metal and that of transparent substances having a high index of refraction has already been recognized by Airy and McCullough. If the small particles of the metals are transparent and have a higher index of refraction than diamond, we have got round the difficulty that shocked those investigators, that one must postulate considerable absorption for the diamond. Long ago, people calculated the indices of refraction of the metals from measurements of polarization and found very high values, 3.06 for copper, 3.9 for gold, 4.86 for silver, etc. In flat contradiction with this are the low values, sometimes less than one, obtained from studying the transmission of light through thin metallic films. Our theory clears this up, because the low indices of refraction are not the indices of refraction of the metals but of the medium between the 'smallest' metallic particles.

"Our assumption also explains the peculiar fact that the absorption increases much less rapidly than the length of path when light passes through a metal film at an acute angle with reference to the plane of the metal. It is also in good accord with our assumption that light receives an acceleration on passing perpendicularly through a metallic film, just as though passing through an optically thinner medium, although the difference in path (according to Quincke is greater than the thickness of the metal film. According to our theory the light passes to an almost negligible extent through the metal itself and chiefly through the interstices and not by the shortest path through these. Quincke[1] had also shown that when a transparent silver or gold film is placed in the path of two interfering sheafs of rays, a displacement of the interference bands occurs which does not correspond to the displacements to be expected from strongly absorbing substances; but is what one would expect if the metal were an ordinary transparent substance, with an index of refraction less than one. This is exactly what follows from our theory.

"In like manner we can explain why the color of the light passing through the metal is not definite but depends on side factors which ordinarily have no special effect on the transmission color of absorbing substances. Silver, which is yellow by transmitted light, can be changed to blue by pressure alone. In the same way a gold which is red by transmitted light can be changed to green. If we were simply dealing with a slight change in shade, this would not be especially significant because other absorbing substances undergo slight changes in color. Here, we are dealing with a change which is almost to the complementary color. Similar color changes can be brought about by long exposure to the air or by contact with substances which can form no possible chemical combinations with the metal. Silver, which is blue by transmitted light, can be converted into yellow silver merely by contact with acids which do not attack the silver at all. The fact that the color of the transmitted

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[1] Pogg. Ann. 129, 186 (1866).

light can vary so much with any one metal—silver can be blue, violet blue, reddish violet, yellow, and gray, while gold can appear reddish, violet, brown, green, and bluish green—must convince us that we are not seeing the real color of the metal. According to our point of view, the color that we see is only the haphazard result of a number of refraction stages which have been turned, through total reflection, more than a right angle from the original angle of incidence and have eventually come out of the metal. The final result is of course dependent on the thickness of the metallic film, on the optical density of the medium in the interstices, and on the change of refraction at the outer medium. This accounts for the change in color through pressure or through contact with indifferent acids.

"The real absorption or (transparent) body color of the completely transparent 'smallest' particles of the metal is not the light transmitted by thin films of the metal but the color of the reflected light. The single particles of gold or brass (there are no copper and zinc molecules in brass), are very pale yellow and those of copper are tinged very slightly reddish. The full yellow or red color is the result of cumulative absorption through many particles. The very faint color of the single transparent particles is also the reason why the few metals having a marked color, such as gold, copper and strontium, have so slight coloring power in alloys and amalgams. They behave like dilute glazing colors. They remind one of such painter's colors as carmine, sap green, and Prussian blue which would be almost black in relatively small pieces if they had tremendous coloring power. If the color of the metals corresponded to a covering body color, an entirely different behavior would be expected.

"We must now consider the previously-asked question, why we only have red and yellow metals in at all saturated colors and not green, blue, and violet ones, in spite of the fact that there is nothing to prevent metallic luster appearing with colors corresponding to the medium and shorter wave-lengths, as we can see with the artificially colored bronzes, with the natural, metallically lustrous, birds' feathers, etc.

"If the small particles of the metals are transparent crystals with a high index of refraction, the rays of long wave-length will undergo total reflection less readily than those of shorter wave-length, and will therefore penetrate deeper into the innermost parts of the metal before they are switched to a direction differing more than ninety degrees from the angle of incidence. If there is at the same time a selective absorption (which will be very slight for the single particles and not very much in all, because otherwise the metals could not show so high reflection coefficients), the loss of intensity will always be greater with the colors corresponding to the medium and shorter wave-lengths. They are therefore absorbed more strongly. If a metal absorbs the shorter wave-lengths, the mean depth, from which the light comes that is apparently reflected, is relatively large and the absorption is relatively marked; the colors corresponding to the longer wave-lengths preponderate markedly. If however the longer wave-lengths are absorbed, the mean depth of reflection and therefore the loss in brightness and color are less. The behavior is entirely analogous to that of turbid media, in which, on account of the greater scattering of the shorter wave-lengths, these latter predominate in the reflected light and the former in the transmitted light. According to our theory the light apparently reflected by the metals is really chiefly transmitted. We get the colors corresponding to the longer wave-lengths by 'reflection' from the metals, just as by transmission through turbid media (red, setting sun). The shorter wave-lengths have a chance to be seen only by 'apparent transmission' through the metals (corresponding to the reflected light of the blue sky)."

This is all extraordinarily bad. Kirschmann says, p. 601, that if metallic luster is due to reflection from the surface of the metal, the high intensity of metallic luster makes it necessary to ascribe to metals practically a zero transparency, which is impossible because there are no absolutely opaque substances. This is merely a play on the word zero. While it is true that the physicists are very vague as to why we should have selective reflection, which is what we get with metals, there is no question in anybody's mind but that selective reflection is intimately connected with intense absorption, of the light reflected selectively.[1] If a dye in solution absorbs green strongly and appears purple by transmitted light, the solid dye is likely to reflect green light selectively. "Not all absorption bands exhibit the phenomenon of quasi-metallic reflection, and it is of interest to inquire into the conditions governing its appearance. Absorption results from resonance vibration of the electrons, but in some cases they throw practically all the energy back, and there is little or no true absorption." This is perhaps what Kirschmann had in mind when he says that "it must then be opacity which is not due to absorption." As a matter of fact, the metals do behave like very opaque substances for certain wave-lengths; but there is quite a difference between extremely high opacity and zero transparency.

We cannot tell some of the crystallized sulphides from metals by their outward appearance. Kirschmann should have gone on and deduced that they were extremely transparent. A necessary consequence of his point of view is that many of the dyes are extremely transparent for the wave-lengths to which they are most opaque in solution.

The paragraph, p. 601, about awakening 'the slumbering metallic luster' of a polished metallic mirror is very misleading. Black glass is nothing like so opaque as a metal and consequently one not only gets less light reflected from it, but the light is reflected from varying depths and therefore gives one the sensation of vitreous luster, which Kirschmann for some unknown reason calls fatty luster. While nobody has ever tried it, it is practically certain that the difference would not have occurred if Kirschmann had compared a metallic mirror with a suitable sulphide mirror instead of with a silicate mirror. Also, the statement about graphite is a half-truth. It is a perfectly simple matter to make a graphite surface which will look silvery, when viewed at a proper angle, and which cannot then be told from a metal.

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[1] Wood: "Physical Optics", 409, 440 (1911).

Kirschmann postulates, p. 602, that "the smallest particles of the metals are completely transparent grains having a very high index of refraction." It used to be considered that the metals had very high indices of refraction; but no physicist believes that now so far as we can learn. In the same paragraph there is another unfortunate statement. "It is also quite irrelevant to our argument what assumptions people make over the transmission of light and especially at the surface of two media. The indisputable part of the wave-theory of light is in the periodicity of the process." The last of the two sentences is intended to show something; but it has no apparent bearing on anything, because there is nothing in Kirschmann's theory which is either helped or hindered by light being a periodic phenomenon. Except for the psychological effect Kirschmann might equally well have said that it is an indisputable fact that the Great Pyramid is in Egypt.

Kirschmann assumes, p. 602, that metals are the most transparent of substances, and that, in the uppermost layer of crystals, a portion of the incident light is reflected totally as in the case of the diamond. Now the striking characteristic of the diamond is not its metallic appearance. On the other hand one does get metallic luster with exfoliated mica; but this requires a laminated structure with very distinct air films between the mica plates. We do not get the effect with the mica until it has been heated. A suitably laminated diamond would undoubtedly be silvery, though there is apparently no record of such a stone having been found. There is also no evidence that cast metals have any laminated structure sufficient to give rise to the optical phenomena actually observed.

Kirschmann's theory accounts for the elliptical polarization of light by metals, which is unfortunate, because the general opinion nowadays seems to be that elliptical polarization is not a characteristic of metals; but is due to an oxide film. Kirschmann is therefore in the awkward position of accounting for the occurrence of a non-existent property.

Kirschmann postulates, p. 604, that the apparent "low indices of refraction of the metals are not the indices of refraction of the metals but of the medium between the 'smallest' metallic particles. Unfortunately he gives us no clue as to the nature of the 'medium' having these low indices of refraction. We do not even learn whether there are different media in different metals.

Kirschmann hails as a triumph for his theory, p. 604, the fact that the transmission color of silver may be blue, reddish violet, or yellow; and that of gold may be reddish [why not red?], violet, brown, green, or bluish green. He considers that these colors are the haphazard results of a number of refraction stages; but he has entirely overlooked the fact that these color changes do not occur with massive gold or silver; but only when we have them in a granular or colloidal state. He is therefore accounting again for a non-existent phenomenon. If a theory only enables its originator to predict things which are not so, it cannot be considered a good working hypothesis. Kirschmann is apparently forced, p. 606, to consider all substances showing metallic luster as turbid media. That speaks for itself.

The remainder of Kirschmann's paper deals with experimental data and is extremely interesting. "The test of the accuracy of the theory is easy to make. If metallic luster is parallactic in nature, the phenomena in question depending on the parallax of indirect vision, and if metals consist of very transparent particles, it must be possible to create metallic luster by means of non-metallic less highly refractive, transparent substances, provided we can reproduce the necessary conditions for the production of the parallax of indirect vision. The light reflected from a point on the surface must consist of components having a difference of path sufficient to be important in the parallax of indirect vision and yet not so great as to give rise to the binocular and displacement parallax which we have with the ordinary surface luster. We cannot duplicate artificially either the high index of refraction of the hypothetical, small, metallic crystals nor their arrangement in space of which we can only assume that within certain limits it cannot be changed optically by intermolecular processes (temperature change, etc.), at least, so far as our direct cognition shows. We cannot therefore duplicate the high reflecting power of metals artificially. We have seen previously that the great intensity of the reflected light is a very frequent accompaniment of luster in general and especially of metallic luster; but that it is not really essential to all true (parallactic) luster. We are therefore justified in not attempting to duplicate metallic luster in its full intensity and we can confine ourselves to obtaining conditions for intensifying the parallax of indirect vision on an apparently homogeneous surface. The simplest way of doing this is to pile up enough thin plates which reflect on the front and back sides, the number of the plates being such that their total thickness does not give rise to any direct (binocular, etc), consciousness of depth. The thinnest glass plates which can be obtained are much too thick for this purpose. Very thin, completely transparent, gelatine films, if combined in sufficient number, show a distinct metal-like luster. Excellent results can be obtained by using water-clear mica. Mica can easily be split into films 0.010-0.005 mm in thickness or less; but films 0.02-0.08 mm in thickness are the best because the thinner ones do not remain plane and are apt to stick together. Also, when they become too thin they begin to show interference colors, the colors of thin films, because of the difference in phase of the two reflections, one from the top and the other from the bottom of the film. If one piles up thirty to forty films, none over 0.02 mm or under 0.005 mm in thickness, the combination has a luster like smooth tin. In such a sample and in tin also, we do not get pure metallic luster, but metallic luster plus surface luster. The surface luster can be eliminated easily by grinding a matte surface on the uppermost film thereby producing diffuse reflection. We then get the true metallic luster of matte silver. The matte-grinding can be done most easily by shaving with a sharp knife and then rubbing the surface with mica powder and oil or vaseline. Different grades of surface roughening can be obtained by a coarser or finer shaving. One can even imitate file-marks, etc, very successfully. If the mica was colored to some extent originally, the color of the pseudo-metal will vary similarly from a pure white. There is a sort of very brown mica, which gives a preparation having a bronze color. To imitate differently colored metals I have previously[1] used ready-made, colored gelatine sheets such as are made for light-filters, etc. This commercial gelatine is however colored too strongly, besides not occurring in the right shades. It is also rather too thick and usually somewhat lacking in transparency. I have therefore worked out another process which gives much better results. By dipping sheets of mica in a bath, I coat them with a very thin film of slightly colored gelatine. The sheets remain completely transparent and the color can be varied at will both as to intensity and shade. By a suitable choice of the color and number of these sheets, it is possible to imitate in an extraordinary fashion the red and the yellow metals, and also the more delicate shades of the nearly colorless ones. A number of samples of these pseudo-metals can be seen at any time in the author's laboratory in the Psychological Institute of the University of Leipzig.

"Nature produces colors in the same way, quite apart from the previously-mentioned, metallically lustrous colors on animal bodies, in the metallically lustrous gall-stones which are not interference colors due to the thinness of superposed laminae deposited from urine as Brücke assumed; but are the result of the parallactic relations which we have been discussing. This is probably also the case with the apparently golden teeth of many chamois which are wont to drink the Alpine waters, containing quite an amount of sparingly soluble calcium and magnesium salts. The numerous thin films of the urine deposits and of the salt precipitated on the teeth behave exactly like our thin sheets of mica. Mica, which has been separated a little by weathering has a certain luster like silver which has caused it to be known as cat silver. After pieces of mica have been heated white-hot, they show metal-like luster. Metallic luster obtained in this way is by no means so good as that in the mica samples just described.

"The metal-like luster on the surface of many strongly-absorbing dyes like fuchsine, carthamine, indigo, and cyanine must not be overlooked. This luster is due to the fact that light is reflected from different depths. The difference in depth of the different components is probably much less than in the real metallic luster, which is why the effect is less intense. On account of the very strong absorption, the reflection is very weak in comparison with that of metals. There is another great difference between these metallic-like, lustrous, surface colors and the colors of metals. The latter are, as we have explained, the actual body colors of transparent substances. They correspond therefore to the red of the fuchsine and the blue of the indigo, to the light transmitted by these substances. The colors of the solid dyes are real surface colors and represent that portion of the untransmitted light which is not absorbed but is reflected from the surface layers for some reason. These colors correspond therefore to those transmitted by thin metal films. In accordance with this reversal of the relations are the phenomena of anomalous dispersion. While

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[1] Wundt's Philosophische Studien, 11, 147 (1895).

these consist in the metals in a simple reversal of the order of the colors, which, according to our view, may not be abnormal, the highly absorbing dyes with the metal-like surface luster, show typical anomalous dispersion with characteristic absorption bands and with the change in the refractive indices at the limits of the absorption bands. I should like also to call attention to the fact that the peculiar luster of these substances is more like the metallic luster of animal bodies than like that of the actual metals or that of the mica preparations."

The mere fact that so much of what Kirschmann says is wrong is not in itself conclusive proof that he is wrong throughout. His chief thesis is that metallic luster is due to the parallax of indirect vision, which sounds well but is not especially helpful. It is apparently based on Wundt's theory that luster occurs when one sees or thinks one sees one image behind another. If that proves wrong, everything goes. That question will be considered in the second paper. Whether right or wrong, Wundt's point of view seems to have very little pragmatic value because nobody, not even Kirschmann, has applied it to the different cases of metallic luster which actually occur, nor has anybody showed that it can be so applied.

It was not possible to ignore Kirschmann's paper in spite of its many errors because Kirschmann is a pupil of Wundt's and a professor in the psychological institute at Leipzig, and because Wundt has spoken approvingly of his earlier work which was along the same line as the 1921 paper. In other words Wundt was apparently behind Kirschmann and Wundt's name is one to conjure with. In fact, Kirschmann's paper was called to our attention by a professor of psychology as representing the very latest thing in the way of scientific progress in the study of metallic luster. Of course that was an exaggeration; but Kirschmann's paper never could have been published if anybody had realized how extraordinarily bad it is. It was therefore necessary to justify our opinion at some length.

Cornell University.

THE MOLECULAR LOWERING OF THE FREEZING POINT OF LIQUID AMMONIA[1]

BY LOUIS D. ELLIOTT

Introduction

The development by Franklin and coworkers of the ammonia system of compounds in which liquid ammonia occupies a position analogous to water in our familiar water system has opened up an extensive field of research. Step by step the parallel relationships between ammonia and water have been brought out by numerous investigations of reactions in liquid ammonia as a solvent and through studies of the physical properties of this remarkable substance.[2]

It was for the purpose of contributing to our knowledge in the latter field that the work upon the molecular lowering of the freezing point of ammonia was undertaken.

No direct determination of the freezing point constant has hitherto been made. From the fact that the boiling and freezing point constants for water, 5.2 and 18.6, respectively, are relatively very low, and that the boiling point constant for ammonia,[3] 3.4, is the smallest known we should expect the cryoscopic constant for ammonia to be even smaller than that of water. Massol's[4] value of 1838 calories per gram molecule for the heat of fusion of ammonia and that of de Fourcrand and Massol[5] of 1950 lead to the calculated values of 7.1 and 6.6, respectively, for the molecular lowering of the freezing point of ammonia. The work of Rupert[6] and that of Postma[7] on the freezing point curve of the system water-ammonia, though not involving precise differential temperature measurements do, however, indicate a value, in the case of water as solute at least, only slightly under 10 for the more dilute solutions measured.

Thermometry

A consideration of the thermometric methods available in low temperature measurements led to the conclusion that platinum resistance thermometry would lend itself most satisfactorily to the accurate measurements of small temperature changes in the temperature region involved.

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[1] From a thesis presented to the Department of Chemistry and the Committee on Graduate Study of Stanford University, August 1923, in partial fulfillment of the requirements for the degree of Ph.D.

[2] Some of the important papers in connection with this development are: Franklin and Kraus: Am. Chem. J., **20**, 820 (1898); **23**, 277 (1900); Franklin and Stafford: **28**, 83 (1902); Franklin and Cady: J. Am. Chem. Soc., **26**, 499 (1904); Franklin: **27**, 820 (1905); Franklin and Kraus: **27**, 191 (1905); Franklin: Z. physik. Chem. **69**, 272 (1909); Franklin: Am. Chem. J., **47**, 285 (1912); Franklin: J. Am. Chem. Soc., **44**, 185 (1922).

[3] Franklin and Kraus: Am. Chem. J., **20**, 836 (1898).

[4] Compt. rend. **134**, 653, (1902).

[5] Compt. rend. **134**, 743 (1902).

[6] J. Am. Chem. Soc., **32**, 748 (1910).

[7] Rec. trav. chim., **39**, 515 (1920).

As no suitable resistance thermometer was available it was thought worth while to design one suitable for accurate measurements under the conditions involved which could be constructed out of materials at hand. Although nearly all successful forms of platinum resistance thermometers have been of the mica cross type[1] it was thought advisable to discard the mica cross feature and to construct a glass core thermometer which could be made by a glass blower with the fewest materials possible. Since the practice of imbedding the wire by fusion into the glass core as in the Heraus and de Leeow type instruments[2] is undesirable from the standpoint of possible strains[3] in the winding it was decided to wind the wire loosely upon a glass core and protect it with a glass sheath.

Thermometer No. 4 which was used throughout this investigation was constructed as follows: For the core A, Fig. 1, ordinary soft glass tubing eight millimeters outside diameter, coated with paraffin, was placed in a lathe and double threads fifty to the inch, cut through the wax. By etching with hydrofluoric acid very satisfactory threads around the glass were obtained. The thermometer core was made from a section of this tube about four centimeters long which was fused shut at one end. The platinum resistance wires, fused to the silver lead-wires L[4] (shown without their protecting tubes), threaded through the two small holes F situated 2.5 centimeters from E and fixed in position by two minute drops of fused lead glass were non-inductively wound upon the threads etched in A. The ends of the resistance wires were then fused together and held in position at E by means of droplets of fused lead glass. The silver lead-wires were insulated from each other by placing in narrow bore thin-walled glass tubes. To obviate air currents up and down the stem of the thermometer these three tubes passed through a small cork (not shown in Fig. 1) of such a diameter as to fit snugly in the glass stem tube B. A thin-walled glass sheath C of the same diameter as B (2 cm) was placed over the core and sealed to B at H leaving an air space around the core tube of about one half millimeter thickness. The platinum resistance element on the core consisted of approximately 100 centimeters of pure platinum wire 0.0075 millimeters in diameter the length chosen being such that the resistance of the thermometer at 0° would be in the neighborhood of twenty five ohms. With such a resistance a reading of 0.0001 ohms on the bridge employed would correspond to approximately 0.001°. The wire was flash annealed before and after winding. Within the

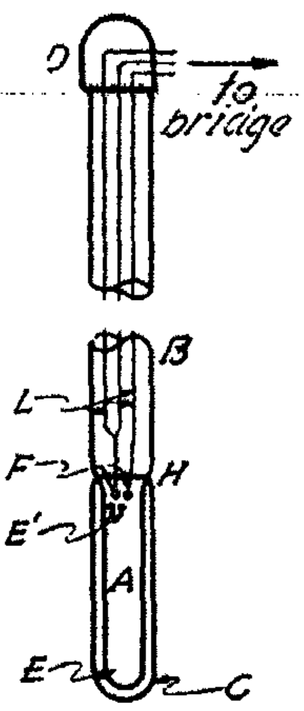

FIG. 1

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[1] Callendar: Phil. Mag., 32, 104 (1891); T. S. Sligh: Bur. Standards, Scientific Paper No. 407 (1921); J. Am. Chem. Soc., 43, 470 (1921).

[2] De Leeow: Z. physik. Chem., 77, 304 (1911).

[3] Sligh: loc. cit.

[4] W. Siemens: Proc. Roy. Soc., 19, 351 (1871); Waidner and Burgess: Bur. Standards Bull. 6, 152 (1915).

glass head D, fitted over the stem tube B with sealing wax, the silver leads were soldered to insulated stranded lamp cord wires which served as the three external leads to the bridge. Entrance of these external leads to the head was effected through three holes in the side of the latter made tight with sealing wax. The total length of the thermometer was about 35 centimeters. Resistances were measured upon a five-dial Leeds and Northrup Mueller type precision temperature bridge[1] using a highly sensitive d'Arsonval mirror galvanometer with lamp and scale. The bridge having been adjusted to accuracy by the manufacturers was not further calibrated for this work.

Resistance—Temperature Relationships

Between −40° and +1100° the relationship between temperature and the electrical resistance of pure annealed platinum is accurately expressed by Callendar's parabolic equation of the form; $R = R_0(1 + \alpha t + \beta t^2)$.[2] Below approximately −40° the relationship begins to deviate from this law.

From Henning's calibration[3] of a platinum resistance thermometer against a hydrogen thermometer it was shown that the above equation gives temperatures 0.08° too low at −78° and over 2° too low at −193°. The curvature of the deviation curve at −77°, that is, the rate of change of deviation from the Callendar formula is too great to allow of the use of interpolated corrections in this temperature region.

Rather than attempt to use any of the several equations of higher degree it was decided to make use of a relationship found by Henning connecting the resistance of any two thermometers. In order to use this relationship it was necessary to calibrate our thermometer at only one point, preferably at liquid air temperature, other than the ice and steam points. From the value for the resistance at 0° (r_0) we could derive the *resistance ratio* (R_t) of our thermometer, that is, the ratio of its resistance (r_t) at a specified temperature to its resistance (r_0) at 0°. Henning carefully calibrated a standard platinum resistance thermometer, P. T. R. No. 32, against a hydrogen thermometer in the interval between −193° and +7° thus connecting the resistance ratio (R) of his thermometer to temperature. It now only remained to find a functional relationship between the resistance ratio of our thermometer and that of No. 32. This was accomplished by using the relationship found by Henning to exist between the resistance ratios of any two thermometers expressed by the formula:

$$(1) \quad R_1 - R = M(R-1) + N(R-1)^2, \text{ in which}$$

$$M = \frac{a_1}{a}(1 - 100c) - 1, \text{ and}$$

$$N = \frac{a_1 c}{a^2}$$

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[1] For a description of this type of bridge see Mueller: Bur. Standards Bull. **13**, (1917); Waidner, Dickinson, Mueller and Harper: Bull. **11**, 571 (1915).

[2] Callendar: Phil. Trans. **178** A, 161 (1887); Sligh: loc. cit.

[3] Henning: Ann. Physik, (4) **40**, 635 (1913).

a and a_1 are the fundamental coefficients of No. 32 and our thermometer, respectively, obtained from ice and steam point calibrations.

(2) $a = \dfrac{r_{100} - r_0}{100 r_0}$ in which r_{100} = resistance at 100°. c, a constant determined by calibration of our thermometer at liquid air temperature is found by means of the equation:

$$(3) \qquad c = \frac{\dfrac{R_1 - 1}{a_1} - \dfrac{R - 1}{a}}{\dfrac{R - 1}{a}\left(\dfrac{R - 1}{a} - 100\right)}$$

This may be put into a more convenient form by using the concept of "platinum temperature" (pt) which is related to resistance by the linear equation:

(4) $pt = 100\dfrac{r_t - r_0}{r_{100} - r_0}$, r_t being the resistance at the temperature in question. Equation (3) now becomes:

(5) $c = \dfrac{pt_1 - pt}{pt(pt - 100)}$, in which pt_1 = platinum temperature of our thermometer and pt = platinum temperature of standard thermometer. Having determined R_1 experimentally R may be calculated and the corresponding temperature obtained from Henning's table of values of R.[1]

Calibration of the Thermometer

The steam point of our thermometer was determined by the usual hypsometer method.[2] The value for the resistance at 100° (r_{100}), 32.3433 ±0.0004 ohms was arrived at by averaging five values, corrected to standard conditions, obtained on five different days, and calculating the probable error.

The ice point was determined as follows; an ice sheath of inside diameter slightly larger than the diameter of the thermometer was made from distilled water and the sheath surrounded with shaved commercial ice. The sheath was filled with distilled water cooled to 0° and the thermometer inserted. From a series of thirteen readings agreeing to within 0.002 ohms the value for the resistance at 0° (r_0) was determined to be 23.2811 ohms with a calculated probable error of 0.0001 ohms. Upon recalibration at the ice point after six months the resistance was found to be unchanged. From these two calibrations the characteristic constants for thermometer No. 4 were derived. F. I. (fundamental interval), $r_{100} - r_0$, was found to be 9.0622 ohms and a, the fundamental coefficient, F I/$100 r_0$ is 0.003892. The fundamental coefficient of a platinum thermometer is a criterion of the purity of the platinum and should not be less than 0.00388.[3]

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[1] Ann. Physik, (4) **40**, 635, Table 9.

[2] Winkelmann: Handbuch der Physik, **3**, **I**, 22.

[3] Bur Standards, Scientific Paper No. 407, p. 52.

The calibration at liquid air temperature was carried out by the vapor pressure method of Henning[1] for the boiling point of liquid oxygen, the oxygen being purified by the method of von Siemens[2]. As the temperature of the liquid air bath surrounding the bulb of liquid oxygen rose slowly a series of vapor pressure readings for the oxygen were taken as shown in the table below. The pressure readings were made upon a wood scale calibrated with a cathetometer.

Time in minutes	Corrected pressure in mm.	Resistance in ohms	Calculated temperature
7	331.8	5.0936	−190.22°
22	335.9	5.1030	−190.11
31	337.8	5.1135	−190.06
37	337.8	5.1148	−190.06
41	339.3	5.1158	−190.04

The temperature was calculated from the vapor pressure equation of von Siemens:

$$\log p = -\frac{399}{T} + 1.75 \log T - 0.01292\,T + 5.0527,$$

in which p = pressure in millimeters and T = absolute temperature.

Solving equation (5) $c = 5.01 \times 10^{-7}$. N therefore becomes negligible and drops out of equation (1), and M becomes −0.0056, hence $R = \frac{R_t - 0.0056}{0.9944}$.
To expedite conversion of resistance to temperature a table of corresponding R_t values covering the range of temperatures involved was made, thus allowing the temperature corresponding to R_t to be read off from our table directly.

Description of Apparatus

The apparatus as finally adopted and used throughout the work is shown diagramatically in Fig. 2. The Dewar vessel A, the inside dimensions of which were 33×8.5 centimeters served as a container for a cooling bath of petroleum ether. The receptacle for holding liquid air, the refrigerant employed, was a pyrex bulb B suspended in the ether bath by its entrance and exit tubes C and C′, respectively, which passed through the cork stopper F as indicated. The lower half of bulb B was made double walled though not evacuated. A preliminary bulb, double walled nearly to its top did not permit of rapid enough heat transfer, while with the bulb adopted the temperature of the bath and apparatus could be quickly reduced to the desired region by keeping it full of liquid air. When maintaining a constant temperature a little liquid air in the lower part was sufficient. The freezing cell D (28×3 centimeters) is shown in place, separated from the bath by its air mantle tube E. This gave an air space around D of five millimeters thickness which was found to give a very satisfactory rate of cooling. The side tube of the cell was closed

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[1] Ann. Physik, (4), **43**, 282 (1913); Bergstrom: J. Phys. Chem., **26**, 363 (1922).

[2] Ann. Physik, (4) **42**, 871 (1913).

with a phosphorus pentoxide drying tube. The petroleum ether was agitated by means of a very efficient stirrer (omitted in Fig. 2) consisting of a brass cylinder (25×2 centimeters) within which a rapidly revolving brass rod equipped with small propellor blades at three intervals drew the liquid in through apertures near the bottom and forced it out at the top of the cylinder near the surface of the ether bath. The temperature of the bath was observed on a pentane thermometer (not shown in the figure)passing through stopper F. Passing through the cork stopper Q of the freezing cell were the resistance thermometer, G, a platinum stirrer (omitted in the figure), and the small tube H of capillary dimensions for introducing the solvent. The platinum stirrer consisted of a stiff platinum rod which passed through the mercury seal as indicated at I and extended to the bottom of the freezing cell. Near the lower end three platinum rings were fastened to the rod in a horizontal position at intervals in such a way as to thoroughly stir the ammonia solutions. The up and down motion of the stirrer was effected by means of a suitable pulley belted through gear reducing wheels to a motor. In order to melt the crystals of ammonia after each freezing point reading, a coil of platinum wire was fused into the bottom of the freezing cell, the copper leads to which it was soldered passing up through the air jacket and to the outside between R and D. A coil of No. 30 enameled manganin wire about 60 centimeters long, was wound around the upper portion of the cell so that heat might be applied to loosen

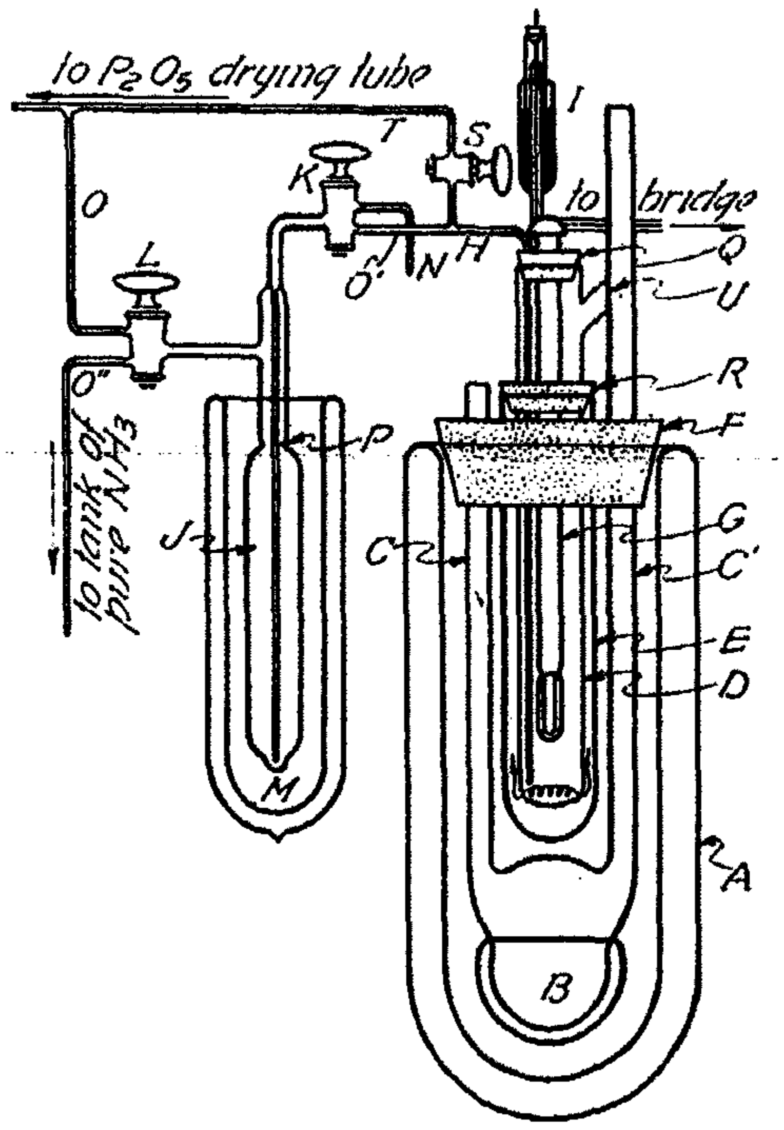

FIG. 2

slight crusts of ammonia crystals which tended to form at the surface of the ammonia. The three terminal wires from these two separate heating coils were attached through suitable switches, a variable rheostat and ammeter to a source of potential.

The calibrated ammonia-filling pipette J was attached by means of the two-way stopcocks L and K to the tubes O and O′ in such a manner that dry air could be by-passed around J through stopcock S and allowed to circulate through the freezing cell or could be made to force the ammonia sample from J into the freezing cell. The Dewar tube M containing commercial ammonia was used as a bath for J when distilling dry ammonia from a ten-pound steel bomb into J through O″. Before attaching to the apparatus by fusing at O and O′ the filling pipette J was calibrated with water and its volume to the tip of the pointer P found to be 80.8 cubic centimeters. Assuming the density of liquid ammonia at −33.3° to be 0.682,[1] the weight of the ammonia to the pointer while surrounded with a boiling ammonia bath was calculated to be 55.1 grams.

The three lead wires from G were connected with the bridge and galvanometer and the readings made as described in connection with the calibration of the thermometer. After each run the introductory tube was severed at H and the apparatus disassembled for cleaning. After reassembly preparatory to a new run the introductory tube was resealed to the pipette and the two corks, Q and R, made tight with paraffin.

Purity of the Ammonia

The ammonia used as the solvent in this investigation was prepared as follows: liquid ammonia from a tank of ordinary commercial ammonia was distilled into the ten pound steel tank containing sodium amide. The tank was connected to J by a lead tube fastened to the glass at O″ by means of sealing wax. Midway of the lead tube a short piece of glass tube containing a little ignited asbestos was interposed to trap any material that might carry over mechanically. After distilling into J the doubly distilled product was considered to be pure and dry.[2] During the course of the work several new lots from the same tank of commercial ammonia were taken and once an entirely new lot was drawn from another cylinder. In no instance could any effect upon the freezing point be detected by the change of source of the ammonia.

Mode of Procedure

Each run consisted of freezing point measurements in increasing concentrations of one solute preceded in each case by a determination of the freezing point of the pure solvent. After filling the Dewar vessel A, Fig. 3, with the bath liquid through a siphon tube inserted through the stopper F (omitted in

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[1] Fitzgerald: J. Phys. Chem., 16, 654 (1912); Cragoe and Harper: Bur. Standards, Scientific Paper No. 420 (1921).

[2] Franklin and Kraus: Am. Chem. J., 23, 285, (1900).

the figure) and starting the bath stirrer, a large vacuum bottle serving as the liquid air reservoir was connected to the inlet tube C by means of a double walled tube evacuated between the walls. Stopcocks L and K were turned to communicate with O″ and N, respectively, and a slow stream of ammonia gas passed through J to sweep out moisture and air. The gas passed out through a rubber tube fastened to N and was caught in a water bottle. At the same time air from the phosphorus pentoxide drying train was passed by way of S and H into the bottom of the freezing cell and the current of air maintained while the temperature of the system was being lowered by pumping liquid air into B. In preliminary experiments in which this stream of dry air was omitted there was invariably a deposition of water and consequent ice formation upon the wall of the freezing cell during the cooling period. While cooling was in progress stopcock K was closed and the ammonia bath M brought up around J at the same time. Ammonia from the bomb was then passed into J more rapidly until the pipette was filled to the pointer with the condensed ammonia. Stopcocks L and K were then both closed, M withdrawn, and a similar tube substituted containing petroleum ether temporarily borrowed from A at a temperature of about −100°. After the ammonia was cooled well below its boiling point, the three stopcocks were so manipulated that liquid ammonia was forced into the freezing cell by air pressure. The ammonia was carried to the very bottom of the cell and the small amount of vapor momentarily escaping before the exit was covered was immediately frozen upon the wall of the cell. When transference was complete stopcocks L and K were closed and the ammonia was brought down to its freezing point. The platinum stirrer was started when the solvent was transferred to the cell and a uniform speed of one stroke per second maintained by means of a rheostat interposed between the actuating motor and the stirrer. The length of the stroke was so adjusted that the column of liquid was well stirred the whole of its length by the stirrer rings.

It was found by experience that the best rate of heat transfer was obtained by holding the bath temperature in the neighborhood of −88° to −93°. The supercooling throughout the work never amounted to more than 0.2°. No corrections for concentration due to separation of solid ammonia have been made for the reason that the small amount of observed supercooling taken in connection with the exceptionally high heat of fusion of ammonia gave a corrected value without significance. The lag of the thermometer was very slight, the galvanometer responding to the appearance of crystals within a few seconds. The temperature rise from the lowest reading to the maximum required usually from three to five minutes. It was noted throughout that in the case of the pure solvent the crystals formed had a tendency to adhere to the stirrer or to one another in the bottom of the cell. On the other hand even from the most dilute solutions employed ammonia crystals separated which did not show this tendency and were easily kept in motion throughout the liquid by the stirrer.

In determining the freezing point of the pure solvent and of the subsequent solutions, several readings were taken, melting and recooling between each reading. The application of about forty watts of energy to the lower coil for a few seconds usually sufficed to melt the crystals. Although the surface of the ether bath was held at different levels at different times above that of liquid in the freezing cell no effect was noticeable upon the readings. It was usually kept, however, about two or three centimeters above that of the contents of the cell.

Liquid solutes were introduced through the side tube by means of an Ostwald pipette taking precaution that each drop reached the surface of the liquid in the cell. Solid solutes when readily soluble or when small in quantity were added in pellet form. For the larger quantities of solute the small weighing tube A, Fig. 3, was utilized. The tube B, over the lower end of which was fitted the rubber tube C, was weighed with A and the stopper D. When introducing the solute into the freezing cell the tube B was inserted into the side tube so that C reached nearly to the surface of the liquid and the material from A allowed to pass through B and C directly into the solution. After withdrawing B and C and allowing the moisture condensed upon the cold tube to evaporate they were again weighed with A and the weight of the sample thus obtained by difference. In weighing out the larger quantities of solute where it was only necessary to weigh to the first or second decimal this method proved very satisfactory and entirely obviated the possibility of solid solute adhering to the sides of the cell.

To avoid radiation of heat through the Dewar vessel A containing the petroleum ether bath the former was surrounded by a black cloth while readings were in progress. In order to ascertain what effect possible dissolved gases might have upon the freezing point air in one instance was passed through the ammonia in the cell for five minutes. The subsequent freezing point reading agreed with the previous reading to within 0.002°.

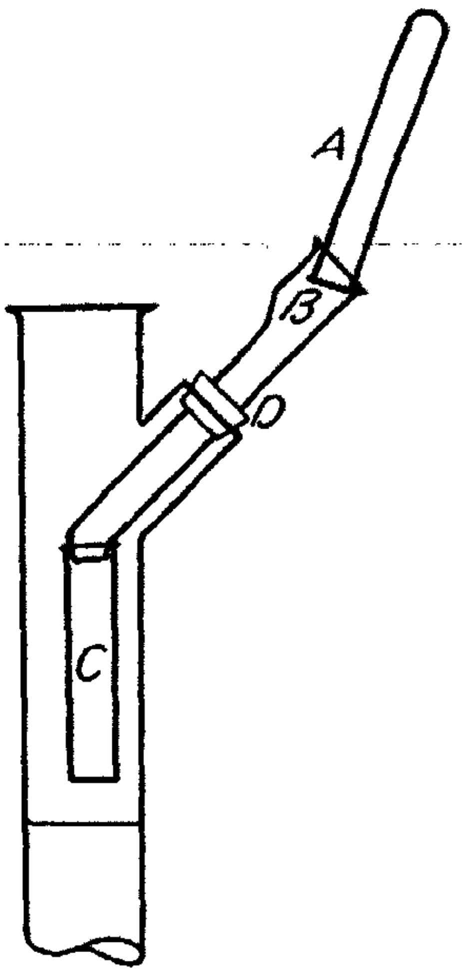

Fig. 3

Accuracy of the Measurements

In considering the accuracy of temperature measurements distinction must be drawn between the absolute accuracy of the temperatures measured and the accuracy of the temperature differences in any one set of measurements. Henning's functional relationship[1] between resistance ratios gives temperatures which are accurate to within about 0.02°. However, the accuracy of the temperatures obtained in the calibration at the boiling point of oxygen, the least accurate of the calibration points, is about ±0.03° and this figure

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[1] Loc. cit. and Ann. Physik, (4) **43**, 282 (1914).

may be considered to represent the absolute accuracy of our measurements. Since the measuring instruments employed were sensitive to differences of less than 0.001° the limiting factor in the accuracy of temperature *differences* becomes the closeness with which conditions may be controlled during any one run. It was found that duplicate readings usually agreed to within 0.0004 ohms. Taking into account the number of duplicate readings made the accuracy of the temperature differences is approximately 0.002°.

Freezing Point of Ammonia

Since each run was preceded by a determination of the freezing point of the pure solvent a series of forty such determinations were obtained whose range of values is shown in the distribution table below. The first column gives the total temperature range of observed freezing points divided arbitrarily into ranges of 0.01°. The second column shows the number of times the freezing point measurements fell into that particular range. From the table it is seen that twenty-nine out of the forty observations agreed to within 0.04°. The average of the forty freezing point temperatures is −77.726°. Taking into account the absolute accuracy of our temperature measurements the value for the normal freezing point of liquid ammonia is found to be −77.73°0±.03°. Employing a platinum resistance thermometer and the regular Callendar formula with Henning's corrections the U. S. Bureau of Standards[1] determined the temperature at the triple point to be −77.70°. Bergstrom[2] calculated the temperature at the triple point from vapor pressure data to be −77.9°.

Table of Freezing Points

Range			Frequency
−77.680°,	to	−77.689°	1
.690	"	.699	2
.700	"	.709	6
.710	"	.719	7
.720	"	.729	7
.730	"	.739	9
.740	"	.749	2
.750	"	.759	3
.760	"	.769	1
.770	"	.779	2

Results of Measurements

The order of accuracy of the measurements of temperature differences made the determination of the freezing point constant in concentrations of less than about 0.006 moles per 100 grams ammonia impracticable. The lower concentrations employed are of the same order of magnitude as those employed by Franklin and Kraus[3] in their work on the boiling point rise of ammonia.

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[1] McKelvy and Taylor: Bur. Standards, Scientific Paper No. 465 (1923).

[2] J. Phys. Chem., **26**, 367 (1922).

[3] Loc. cit.

In the case of nearly every solute two and sometimes three or more series of measurements were made, each series being one day's run consisting, as previously indicated, of the determination of the freezing point of the solvent followed by the freezing point determinations of the solutions of the particular solute under study in increasing concentrations. Tables 1 to 9, inclusive, show the results upon such substances as might be expected to give fairly normal values for the constant at least in the lower concentrations. Table 10 to 16, inclusive, give the data for substances expected to show some dissociating effect of the solvent upon the solute. In the headings for the columns of the tables, g = grams of solute used, M = one hundredths moles per 100 grams

TABLE I

Urea

Series	g	M	dT	K
A 1	0.196	0.593	0.062°	10.5
E 1	0.209	0.634	0.059	9.3
B 1	0.216	0.651	0.066	10.1
D 1	0.219	0.663	0.062	9.4
D 2	0.361	1.09	0.101	9.3
E 2	0.407	1.23	0.113	9.2
A 2	0.440	1.34	0.135	10.1
D 3	0.680	2.06	0.190	9.2
B 2	0.691	2.10	0.201	9.6
E 3	0.697	2.11	0.201	9.5
C 1	0.734	2.23	0.218	9.8
A 3	0.758	2.30	0.231	10.1
E 4	1.006	3.03	0.275	9.1
A 4	1.18	3.56	0.339	9.5
D 4	1.18	3.56	0.328	9.2
E 5	1.51	4.57	0.409	8.9
B 3	1.57	4.75	0.449	9.5
C 2	1.88	5.71	0.524	9.2
D 5	2.00	6.06	0.542	9.0
A 5	2.13	6.43	0.591	9.2
B 4	2.32	7.03	0.677	9.7
E 6	2.50	7.58	0.655	8.7
B 5	2.82	8.53	0.821	9.6
D 6	3.07	9.29	0.815	8.8
C 3	3.40	10.31	0.902	8.8
D 7	3.56	10.8	0.919	8.5
E 7	3.99	12.1	1.014	8.4
D 8	4.05	12.3	1.03	8.4
E 8	4.62	14.0	1.15	8.2
E 9	4.94	15.0	1.23	8.2
C 4	6.08	Solubility exceeded.		

solvent, dT, the observed depression of the freezing point and K, the molecular lowering of the freezing point. The weight of solvent in all cases was 55.1 grams. The value for K was calculated by the equation:

$$K = \frac{\text{gm. solvent used} \times \text{mol. wt. solute} \times \text{depression}}{\text{gm. solute} \times 100}$$

The results upon each solute are tabulated in the order of increasing concentration irrespective of the order of series so as to bring out more clearly the agreement between results of different series. Series are indicated by letter and the individual measurement by number.

Soon after adding C 4 it was observed that the solubility was exceeded and as the temperature continued to fall more urea precipitated until the cryohydric point was reached. From the observed reading at this point and assuming a value for K of 8 at this concentration the concentration of the saturated solution was calculated to be approximately 9.5 grams per 100 grams of ammonia at the cryohydric temperature, −78.9°. In a similar manner the solubilities of some of the other solutes in ammonia at low temperatures were obtained.

The urea employed in Series A was a sample of Kahlbaum's second grade dried in a desiccator. For Series B the same sample was recrystallized from amyl alcohol, the last traces of the latter removed with ether, the sustance recrystallized from absolute alcohol and dried in a vacuum desiccator. In the remaining series a sample of Kahlbaum's "Special" obtained before the war was employed.

TABLE II

Ethyl Alcohol

Series	g	M	dT	K
A 1	0.280	1.11	0.123°	11.1
B 1	0.397	1.56	0.163	10.4
B 2	0.602	2.38	0.237	10.0
A 2	0.663	2.61	0.253	9.7
A 3	1.41	5.57	0.542	9.7
B 3	2.47	9.76	0.924	9.5
A 4	2.74	10.8	1.027	9.5
B 4	4.51	17.8	1.63	9.2
A 5	5.03	19.9	1.82	9.2
A 6	7.97	31.4	2.75	8.8
B 5	8.75	34.5	2.96	8.6
A 7	12.00	47.3	3.91	8.3
B 6	13.58	53.9	4.35	8.1
A 8	14.6	57.7	4.68	8.1
B 7	16.5	65.1	5.13	7.9
A 9	17.5	69.0	5.48	7.9
A 10	22.9	90.3	6.59	7.3

A freshly prepared sample of 99.97% ethyl alcohol was used in the measurements upon alcohol.

TABLE III

n-Propyl Alcohol

Series	g	M	dT	K
A 1	0.487	1.48	0.140°	9.5
A 2	0.878	2.65	0.246	9.3
A 3	1.52	4.60	0.418	9.1
A 4	3.29	9.96	0.844	8.5
A 5	5.67	17.1	1.34	7.8
A 6	9.63	29.2	2.01	6.9
A 7	14.8	44.8	2.75	6.1
A 8	20.8	63.1	3.51	5.6

For the measurements upon n-propyl alcohol the sample employed had been purified by repeated distillation from a sample of U. S. Industrial Alcohol n-propyl alcohol. After standing over calcium oxide for several weeks its boiling point was found to be between 97.0° and 97.3°.

TABLE IV

Acetamide

Series	g	M	dT	K
A 1	0.243	0.748	0.069°	9.2
B 1	0.249	0.767	0.076	9.9
A 2	0.556	1.71	0.165	9.7
B 2	0.556	1.71	0.167	9.8
A 3	1.086	3.34	0.325°	9.7
B 3	2.00	6.17	0.596	9.7
A 4	2.15	6.60	0.638	9.7
A 5	3.95	12.16	1.153	9.4
B 4	4.43	13.62	1.293	9.5
B 5	7.47	23.0	2.23	9.7
A 6	8.05	24.8	2.34	9.4
A 7	10.57	32.6	3.03	9.3
B 6	11.27	34.7	3.29	9.5
B 7	12.57	38.6	3.65	9.5
A 8	14.30	44.1	4.05	9.2

The acetamide was twice recrystallized in chloroform from a post-war Kahlbaum article. The purified product was odorless and melted sharply at 81°. The limit of solubility was not reached but from the sluggishness with which A 8 dissolved it should be not far from that concentration.

TABLE V

Water

Series	g	M	dT	K
A 1	0.387	3.91	0.383°	9.8
A 2	0.870	8.78	0.855	9.7
A 3	1.65	16.7	1.62	9.7
A 4	3.35	33.9	3.29	9.7
B 1	5.76	58.1	5.75	9.9
A 5	6.41	64.7	6.41	9.9
B 2	8.98	90.8	9.35	10.3
A 6	11.45	116.	12.35	10.7
C 1	12.9	130.	14.12	10.8
C 2	13.6	136.	15.10	11.0
C 3	14.6	147.	16.60	11.3

The values in Table V carry the concentration to the neighborhood of the cryohydric concentration for the system $NH_3-H_2O.2NH_3$.

TABLE VI

o-Nitrophenol

Series	g	M	dT	K
A 1	0.946	1.24	0.113°	9.1
B 1	1.362	1.78	0.175	9.8
A 2	1.86	2.44	0.226	9.3
B 2	2.04	2.67	0.259	9.7
B 3	3.03	3.96	0.377	9.5
A 3	3.44	4.50	0.404	9.0
B 4	3.53	4.60	0.434	9.4
B 5	3.73	4.87	0.458	9.4
A 4	5.05	Solubility exceeded.		

The cryohydric temperature was found to be −78.2° and the cryohydric concentration approximately 6.7 grams per 100 grams of ammonia. The sample of o-nitrophenol was purified by recrystallization from absolute alcohol and dried in vacuo at room temperature. The product melted sharply at 44.8°.

TABLE VII

Sucrose

Series	g	M	dT	K
A 1	1.67	0.889	0.076°	8.6
E 1	1.87	0.990	0.086	8.7
B 1	2.01	1.07	0.098	9.2
F 1	2.26	1.20	0.106	8.8
D 1	2.48	1.32	0.121	9.2
A 2	2.67	1.42	0.130	9.2
F 2	3.01	1.60	0.158	9.9
B 2	3.04	1.62	0.146	9.0
F 3	3.25	1.72	0.162	9.4
D 2	3.54	1.88	0.195	10.4
C 1	3.58	1.90	0.220	11.6
F 4	3.59	1.91	0.182	9.5
E 2	4.00	2.12	0.219	10.3
D 3	4.43	2.36	0.239	10.2
F 5	4.87	2.59	0.251	9.7
B 3	5.05	2.68	0.250	9.3
D 4	5.94	3.16	0.330	10.4
F 6	5.96	3.17	0.305	9.6
C 2	5.97	3.19	0.352	11.1
E 3	6.02	3.20	0.332	10.4
D 5	6.66	3.54	0.380	10.7
E 4	8.01	4.26	0.431	10.1

For all the series upon sucrose a sample of J. T. Baker's c.p. sucrose was employed the purity of which had been established in another connection.

TABLE VIII

Aniline

Series	g	M	dT	K
B 1	0.590	1.15	0.136°	11.8
A 1	0.648	1.27	0.113	8.9
A 2	1.26	2.46	0.248	10.1
B 2	1.28	2.49	0.256	10.3
A 3	2.48	4.83	0.426	8.8
B 3	2.49	4.86	0.490	10.1
A 4	3.36	6.55	0.534	8.2
B 4	3.37	6.58	0.631	9.6
A 5	4.41	8.59	0.753	8.8
A 6	5.50	10.72	0.938	8.8
B 5	5.51	10.74	0.976	9.1
A 7	7.44	14.6	1.236	8.5
B 6	8.91	17.4	1.48	8.5
A 8	9.54	18.6	1.54	8.3
B 7	12.22	23.8	1.94	8.2
A 9	12.76	24.9	2.21	8.9
B 8	16.2	31.9	2.46	7.8
A 10	17.9	35.0	2.68	7.7
B 9	18.3	35.6	2.73	7.7
B 10	21.2	41.4	3.11	7.5
B 11	24.6	48.0	3.51	7.3

Series A was conducted with a redistilled Bausch and Lomb product while in Series B a redistilled sample of Kahlbaum's "zur Analyse" aniline was used. A curious phenomenon noted in connection with aniline was the complete invisibility of the crystals of ammonia while the concentration was passing through the neighborhood of 39 grams per 100 grams of ammonia.

TABLE IX

Pyrocatechol

Series	g	M	dT	K
A 1	0.513	0.846	0.088°	10.4
A 2	1.044	Solubility exceeded.		

The cryohydric temperature was −77.8° and the concentration approximately 1.2 grams per 100 grams ammonia assuming 10.0 for the value of K.

The solubility of this substance is surprisingly low in view of the fact that Franklin and Kraus[1] report it to be very easily soluble in ammonia at higher temperatures.

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[1] Am. Chem. J., 20, 820 (1898).

Discussion of the Results on Non-electrolytes

The outstanding feature of the results on these solutes is the variation of the constant with concentration. In only two cases, that of acetamide and that of ortho nitrophenol are we justified in arriving at the value for the freezing point constant by simply averaging the values obtained in the case of each. Even with acetamide a slight tendency toward association of the molecule with increasing concentration can be detected. With ortho nitrophenol the low solubility prevented an extensive series of measurements.

With urea, ethyl alcohol, normal propyl alcohol and aniline the tendency to associate is clearly brought out by the decreasing value for the constant with increasing concentration. Except in the case of ethyl alcohol this is in agreement with the behavior of the boiling point constant for these solutes as determined by Franklin and Kraus.[1] In the case of ethyl alcohol they obtained a constant value for the boiling point constant through a wide range of concentrations. With normal propyl alcohol and aniline a comparison of our results with theirs shows the tendency of these two substances to associate to a greater degree at lower temperatures. For urea the degree of association for equal concentrations is about the same at the freezing point as at the boiling point of ammonia. Water which gives a constant value for the boiling point constant does likewise in the case of the molecular freezing point lowering up to relatively high concentrations after which a gradual increase occurs.

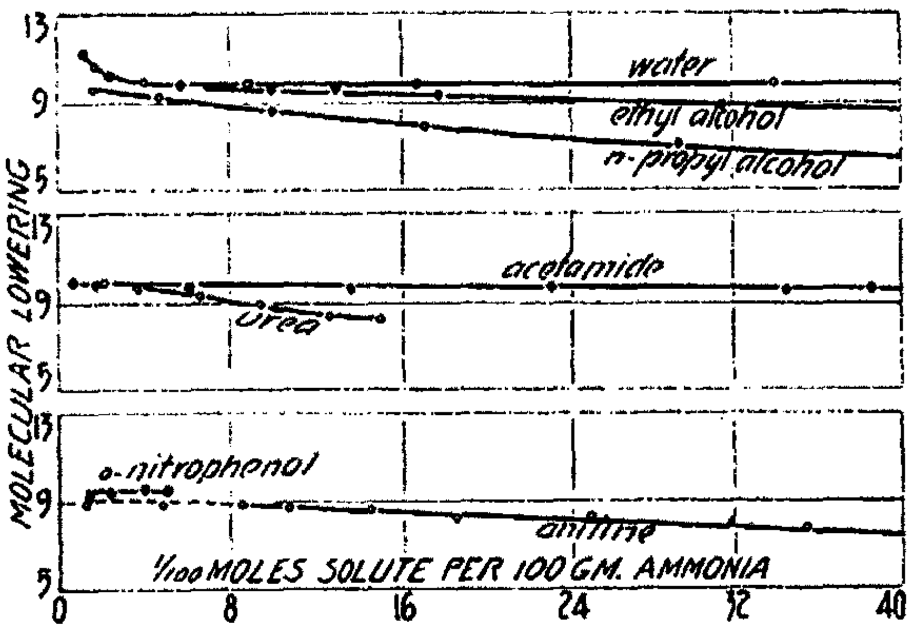

CHART I

The results on sucrose, while unsatisfactory from the point of view of agreement between series, do however, show clearly when considered as a whole a gradual increase beginning with values slightly less than the normal constant. The sluggishness with which the sucrose dissolved after the last few additions of this solute rendered measurements in higher concentration impracticable. The one value obtained for pyrocatechol is of minor significance.

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[1] Loc. cit.

The best means of arriving at the normal value of the molecular lowering of the freezing point is to examine the results on each solute with a view to determining whether or not there is a range of concentrations throughout which constant values occur. In Chart I are plotted the values of the constant against concentration for seven of the nine solutes. It is clear from the graphs that from initial concentration up to that of about 0.06 moles per 100 grams ammonia the constant lies between 9 and 10. With some of the solutes a fairly constant value is maintained up to far greater concentrations. Taking up each solute individually we may proceed to obtain the normal value for the constant.

Urea: Fairly constant values are found up to a concentration of about 0.04 moles per 100 grams ammonia. The average of the first fifteen values in Table I is 9.6.

Ethyl Alcohol: The range of constant values lies between concentrations of about 0.02 and 0.10 moles. While there are not as many points on the curve as in the case of urea the range of constant values is much wider and the results within this range are in closer agreement. The average of the second to the seventh value, inclusive, of the constant in Table II is found to be 9.8.

Normal Propyl Alcohol: Only three values were obtained in concentrations of less than 0.05 moles, the average of which is 9.3.

Acetamide: The average of all the determinations is 9.5.

Water: This solute gives constant values for a wide range of concentrations. The determined points within this range are few but conform closely to a straight line. The average of the first six values in Table V is 9.8.

Ortho Nitrophenol: The average of seven determinations is 9.4.

Aniline: Unfortunately the range of concentrations within which the constant is apparently normal is a range in which individual results were somewhat contradictory. Omitting the first value in Table VIII which appears unreasonably high, the average of the results up to B 4, inclusive, is found to be 9.4.

Leaving out of consideration the above value for normal propyl alcohol based upon too few observation and also omitting the average for aniline we arrive, by averaging the remaining six individual averages, at a value of 9.7 for the normal molecular lowering of the freezing point of ammonia. This is considerably higher than that calculated by Massol[1] from his experimental value for the heat of fusion of ammonia. Calculating back from our freezing point constant of 9.7 by van't Hoff's formula, $W = \frac{0.02T^2}{K}$, we obtain for the value of W, the heat of fusion, 78.7 calories per gram, almost the same as the corresponding value for water, or 1338 calories per gram molecule as against 1838 determined by Massol.

Raoult found that the lowering of the freezing point produced by one molecule of a solute in one hundred molecules of any solvent is very nearly

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[1] Loc. cit.

a constant, 0.63°. By dividing our value of 9.7 by the molecular weight of ammonia we obtain the value 0.57° for Raoult's constant while Massol's data give a value of 0.42°.

Measurements on Electrolytes

Franklin and Kraus[1] noticed that dilute solutions of sodium nitrate, ammonium nitrate, and potassium iodide in liquid ammonia which are good conductors of electricity gave a molecular boiling point rise considerably lower than expected from a consideration of their relatively high conductivities. It was later established by Franklin and Cady[2] from a study of the velocity of ions in liquid ammonia solutions that the dissociating power of this solvent is more in accord with the value for its dielectric constant of 22 than with conductivity data. The high conductivity of electrolytes in dilute ammonia solutions is explained by the relatively higher speed of the ions. Working with more concentrated solutions Franklin and Kraus[3] later found that the molecu-

TABLE X

Sodium Nitrate

Series	g	M	dT	K
C 1	0.247	0.528	0.067°	12.7
B 1	0.470	1.004	0.109	10.9
C 2	0.491	1.05	0.116	11.1
A 1	0.505	1.08	0.138	12.7
B 2	0.582	1.24	0.133	10.7
C 3	0.742	1.58	0.166	10.5
B 3	0.784	1.68	0.173	10.3
C 4	1.044	2.24	0.230	10.3
A 2	1.045	2.24	0.261	11.7
B 4	1.53	3.28	0.337	10.3
C 5	2.03	4.34	0.439	10.1
A 3	2.05	4.39	0.480	10.9
B 5	3.15	6.73	0.690	10.3
C 6	3.53	7.54	0.757	10.0
A 4	3.53	7.54	0.806	10.7
A 5	6.49	13.9	1.49	10.7
C 7	6.53	14.0	1.44	10.3
A 6	8.04	17.2	1.90	11.0
C 8	8.10	17.3	1.86	10.7
B 6	8.16	17.4	1.88	10.8
B 7	10.46	22.4	2.54	11.3

A sample of Kahlbaum's pre-war sodium nitrate was used after drying at 110°.

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[1] Loc. cit.

[2] J. Am. Chem. Soc., 26, 499 (1904).

[3] J. Am. Chem. Soc., 27, 191 (1905).

lar conductivities of these salts in solutions of ammonia were less than in aqueous solutions of the same concentration notwithstanding the greater mobility of the ions.

It was thought of interest to investigate the freezing point depression of these three salts and a few other substances which give good conducting solutions in liquid ammonia. In addition to the three salts mentioned silver iodide and strontium nitrate whose conductivities in ammonia are abnormal were investigated. Two organic compounds, phthalimide and trinitraniline, which give good conducting solutions in ammonia were also included.

Table XI

Ammonium Nitrate

Series	g	M	dT	K
A 1	0.394	0.894	0.133°	14.9
B 1	0.467	1.06	0.140	13.2
B 2	0.668	1.51	0.184	12.2
B 3	0.897	2.04	0.241	11.8
A 2	1.01	2.29	0.269	11.8
B 4	1.26	2.87	0.327	11.4
A 3	1.52	3.46	0.422	12.2
A 4	2.83	6.43	0.747	11.6
B 5	3.91	8.88	0.987	11.1
A 5	4.97	11.3	1.31	11.6
B 6	5.42	12.3	1.41	11.5
A 6	7.87	17.9	2.23	12.4
B 7	9.00	20.4	2.61	12.8
B 8	10.57	24.0	3.17	13.2
A 7	10.63	24.2	3.27	13.5
B 9	12.30	28.0	3.88	13.8
A 8	14.03	Solubility exceeded.		

The cryohydric temperature is −82.03° and the corresponding concentration approximately 25 grams per 100 grams ammonia assuming a value of 14 for K at that concentration.

A sample of J. T. Baker's c. p. ammonium nitrate was recrystallized from water and dried at 110°.

TABLE XII

Potassium Iodide

Series	g	M	dT	K
C 1	0.418	0.457	0.062°	13.5
C 2	0.674	0.740	0.096	13.0
A 1	0.683	0.746	0.099	13.2
A 2	1.15	1.26	0.160	12.7
C 3	1.24	1.36	0.167	12.3
A 3	1.68	1.83	0.222	12.1
C 4	2.04	2.24	0.268	12.0
A 4	2.70	2.95	0.350	11.8
C 5	3.11	3.41	0.397	11.6
A 5	4.07	4.45	0.542	12.2
C 6	6.01	6.57	0.746	11.4
A 6	7.86	8.61	1.042	12.1
A 7	11.1	12.1	1.47	12.1
C 7	12.15	13.3	1.70	12.8
A 8	15.9	17.4	2.28	13.1
C 8	18.3	20.0	2.71	13.5
A 9	20.9	22.8	3.25	14.3
A 10	24.9	27.2	4.11	15.1

A sample of Kahlbaum's potassium iodide was dried at 110°.

TABLE XIII

Strontium Nitrate

Series	g	M	dT	K
A 1	0.510	0.438	0.050°	11.4
A 2	0.789	0.678	0.072	10.6
A 3	1.72	1.47	0.133	9.0
A 4	2.60	2.23	0.170	7.6
A 5	4.24	Solubility exceeded		

For the measurements upon strontium nitrate a sample of Kahlbaum's pre-war anhydrous salt was employed after carefully drying. Upon the addition of this solute to the solvent a strong slaking effect was noticeable, the pellet rapidly swelling and disintegrating to a finely divided form which dissolved very slowly.

TABLE XIV

Silver Iodide

Series	g	M	dT	K
A 1	0.970	0.750	0.061°	8.1
B 1	1.03	0.797	0.066	8.3
B 2	2.13	1.64	0.140	8.5
A 2	2.49	1.93	0.145	7.5
A 3	4.97	3.84	0.278	7.3
B 3	6.24	4.83	0.354	7.4
A 4	10.21	7.92	0.559	7.1
B 4	10.26	7.96	0.581	7.3
A 5	15.9	12.3	0.887	7.2
B 5	16.8	13.0	0.943	7.2
B 6	20.8	16.1	1.165	7.2

The silver iodide for these measurements was prepared by precipitation from potassium iodide and silver nitrate followed by subsequent drying.

TABLE XV

Phthalimide

Series	g	M	dT	K
A 1	0.469	0.579	0.056°	9.7
B 1	0.490	0.606	0.066	10.9
A 2	0.719	0.889	0.093	10.5
A 3	0.853	1.05	0.108	10.3
B 2	0.980	1.21	0.134	11.1
A 4	1.000	1.24	0.130	10.5
B 3	1.240	1.53	0.159	10.4
A 5	1.310	1.62	0.185	11.4
B 4	1.64	2.02	0.212	10.5
A 6	1.69	2.09	0.229	11.0
A 7	1.99	Solubility exceeded.		

The cryohydric temperature was found to be −77.98° and the corresponding concentration approximately 3.4 grams per 100 grams ammonia if K = 11.

A sample of Eastman's highest grade phthalimide which, after drying, melted sharply at 233.5° was used for these measurements.

TABLE XVI

Trinitraniline

Series	g	M	dT	K
B 1	0.686	0.547	0.073°	13.3
A 1	0.727	0.579	0.069	11.9
A 2	1.14	0.908	0.104	11.5
B 2	1.32	1.05	0.107	10.2
A 3	1.60	1.28	0.138	10.8
B 3	2.26	1.80	0.179	9.9
A 4	2.33	1.86	0.187	10.1
A 5	3.02	2.41	0.224	9.3
B 4	3.31	2.64	0.240	9.1
B 5	4.40	3.51	0.303	8.6
A 6	5.11	4.08	0.375	9.2

A pre-war sample of Kahlbaum's trinitraniline melting sharply at 190° was used.

Discussion of Results on Electrolytes

The behavior of the freezing point constant in the case of inorganic electrolytes is shown graphically in Chart II in which the values of K have been plotted against concentration. With sodium nitrate, ammonium nitrate and potassium iodide there is an unmistakable diminution in the value of the constant up to concentrations in the neighborhood of 0.04 moles per 100 grams of solvent followed by a gradual increase. From the dissociation theory the initial decrease is what would be expected with increase in concentration. The minimum values which are between 10 and slightly over 11 for these three salts represent a smaller degree of dissociation at these concentrations than they show in aqueous solutions of the same strength. These values of the constant for good conducting solutions are in accord with the relatively low values found by Franklin and Kraus for the boiling point constant of the same salts.

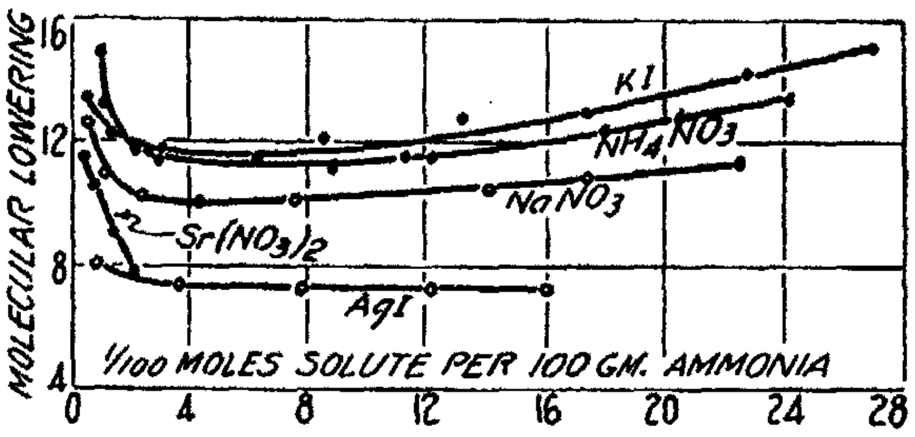

CHART II

No attempt was made to find a quantitative relationship between the degree of dissociation calculated from the freezing point constant and that derived from a consideration of molecular conductivities. The conductivity measurements upon salts by Franklin and Kraus were in general in more dilute solutions than ours. The second investigation of Franklin and Kraus indicating smaller molecular conductivity values in concentrated ammonia solution than in aqueous solution points to the conclusion that the freezing point constant may be quite in accord with the degree of dissociation deduced from probable conductivities at these concentrations. The initial slope of the curves for the freezing point constant of electrolytes in Chart II indicates a rapidly increasing dissociation with dilution.

The gradual rise subsequent to the minimum value of the constant may be explained by assuming the formation of ammonates in solution analogous to the formation of hydrates in aqueous solutions under similar conditions. The curves in Chart II for sodium and ammonium nitrates and potassium iodide show a striking similarity in general form to analogous curves of Jones and coworkers[1] for aqueous solutions of electrolytes. Translating the hydrate theory into terms of ammonia we may state that potassium iodide probably combines with more ammonia in solution than does ammonium nitrate and the latter with more than does sodium nitrate. If the value of K for potassium iodide be calculated upon the assumption of the existence at this temperature of an ammonate, $KI.8NH_3$, the values for K in the case of A 9 and A 10, Table 12, become 9.8 and 9.4, respectively.

Strontium nitrate, with initial values of K indicating a slight degree of dissociation, shows a tendency to rapidly associate with increasing concentration while silver iodide is apparently somewhat associated even at the lowest concentrations measured. The peculiar behavior of these last two salts is reflected in their abnormal behavior with respect to their conductivities in ammonia solution. Franklin and Kraus[2] found that the conductivity of strontium nitrate rises with dilution at a much more rapid rate than that of the other salts studied. Although the freezing point curve for this salt represents a much higher concentration than those employed in the conductivity work yet it suggests a rapid rate of dissociation with dilution. In the case of silver iodide the molecular conductivity was found by Franklin and Kraus[3] to be much lower than for other salts throughout the range of dilutions investigated.

Evidences of slight dissociation of phthalimide persisting throughout the range of concentrations studied is shown by the figures for the freezing point constant.

Trinitraniline behaves more as would be expected showing evidence of slight dissociation at initial concentrations followed by a diminution to fairly constant values slightly below the normal value for the freezing point constant.

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[1] For references to the subject of hydrates in solution see Getman: Outlines of Theoretical Chemistry, 3rd Ed., p. 219 et seq. (1922).

[2] Am. Chem. J., 23, 277 (1900).

[3] J. Am. Chem., Soc., 27, 191 (1905).

Summary

An apparatus has been developed capable of measuring the freezing point depression of liquid ammonia in concentrations of approximately 0.006 moles of solute per 100 grams of ammonia and over.

A glass core platinum resistance thermometer capable of an accuracy, in connection with suitable reading instruments of 0.001° was constructed.

The normal freezing point of liquid ammonia was determined to be −77.73 ±0.03°.

The tendency of substances to associate in ammonia solution renders the determination of the normal molecular lowering of the freezing point of ammonia somewhat difficult. It may be said, however, that in solutions of from 0.006 to 0.04 moles per 100 grams of ammonia 9.7 represents the normal value of the constant. This is considerably higher than that calculated from Massol's value for the heat of fusion of ammonia and suggests the desirability of a redetermination of the latter.

Ammonates appear to be formed in solution in the case of inorganic salts in a manner analogous to the formation of hydrates by salts in aqueous solution.

The data upon the inorganic electrolytes and the organic substances which readily conduct electricity in ammonia solution substantiate the view that ammonia is a much poorer dissociating solvent than water.

In conclusion the writer desires to express his appreciation of the helpful interest and guidance of Dr. E. C. Franklin under whose direction the investigation was carried out.

VISCOSITIES OF SOME MONOVALENT SALTS OF HIGHER FATTY ACIDS IN ORGANIC SOLVENTS

BY MATA PRASAD

In a previous paper from this laboratory Bhatnagar and Prasad[1] have determined the electrical conductivities of some monovalent salts of higher fatty acids in organic solvents and in the fused state. On plotting the equivalent conductivity against dilution in litres they have shown there that the curves obtained are straight lines and not parabolas as required by Ostwald's dilution law. It was first suggested by Wiedemann[2] and later on by Arrhenius[3] that the mobility of an ion is a function of the fluidity of the solution and decreases with an increase in viscosity. Consequently the conductivity of a solution is greatly altered by the viscosity of the solution. The viscosity correction, made by Alemcke and Pissarjewski[4] on the assumption that the conductivity is directly proportional to the dissociation and inversely proportional to the viscosity is of the form—

$$\alpha = \frac{\mu_v}{\mu_\alpha} \cdot \frac{\eta_v}{\eta_o} \qquad (1)$$

where α represents the degree of dissociation, μ_v and η_v, respectively, the equivalent conductivity and viscosity of the solution at the dilution of V litres and μ_α and η_o, respectively, the equivalent conductivity and viscosity of the solution at definite dilution. The same conductivity-viscosity expression was derived by Arrhenius on simple proportionality assumptions.

The present investigation is devoted to the study of the viscosities of the soap solutions in organic solvents and the data so obtained can be utilised to apply the correction to the conductivity values described in the previous paper. Incidentally the results obtained here have also been utilised to verify the various viscosity-concentration relations that have been put forward by Einstein, Hatschek, Smoluchowski and Arrhenius.

Experimental

The soaps used in the investigation were sodium and potassium palmitate, sodium and potassium stearate and potassium oleate. They were prepared by mixing alcoholic solutions of sodium and potassium hydroxides with alcoholic solutions of the corresponding acids in molecular proportion[5]. The alcohols tried were ethyl, normal-butyl and iso-butyl alcohols. They were obtained by distilling Merck's pure alcohols and collecting the fraction distill-

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[1] Cf. Kolloid-Z. 33, 279 (1923).

[2] Pogg. Ann. 99, 228 (1856).

[3] Z. physik. Chem. 9, 495 (1892).

[4] Ibid. 52, 479 (1905).

[5] Cf. Bhatnagar and Prasad: loc. cit.

ing over at the boiling point. Precautions were taken to remove the traces of water by keeping them in soda-lime and quick-lime and afterwards in anhydrous copper sulphate for about a week. They were tested free from aldehyde by the alkali test.

The solutions were prepared by out weighing exactly known quanitites of soaps and dissolving them in known quantities of alcohols. They were kept in glass-stoppered bottles free from contact with air.

The viscosity measurements were made in a viscosimeter of the common capillary pattern of W. Ostwald. The size of the capillary and the volume of the bulb were so chosen that a suitable time of flow of the solutions was obtained. It was about 4 minutes in the case of ethyl alcohol and 7 and 9 minutes, respectively, in the case of n-butyl and iso-butyl alcohols. The viscosimeter was kept in a vertical position by means of two plumb lines hanging from the support holding the viscosimeter. The viscosimeter was kept at a constant temperature at 30°C. All care was taken to remove the traces of grease or impurity in the viscosimeter. In order to achieve this the instrument was washed with soap solution, alkali solution, potassium dichromate mixture and distilled water before and after each observation. The amount of water remaining in the viscosimeter was removed by rinsing it several times with alcohol and drying it in a current of air.

A fixed volume of solution was always introduced in the viscosimeter from a pipette, and after being raised to the upper mark by sucking, was allowed to run through the capillary tube. The viscosimeter was allowed to stand in the bath for a sufficient time to acquire the temperature of the bath, because, as is well known, the viscosity decreases very rapidly with the increase in temperature. The readings were taken when the time of flow became constant which was measured by an accurate stop-watch.

The density of the solutions was measured by means of the specific gravity bottle. The solutions were carefully filled in the bottle and the air bubbles removed from it. It was then kept in the constant temperature bath at 30°C for about two minutes and quickly weighed. From the constants of the bottle determined before hand the specific gravities of the solutions were calculated. The relative viscosities of the solutions with respect to the solvent were then calculated from the formula—

$$\frac{\eta_v}{\eta_o} = \frac{td}{t_o d_o} \qquad (2)$$

where η_o, t_o and d_o are the viscosity, time of the flow and density, respectively, of the solvent and η_v, t and d the corresponding values for the solution.

The viscosity of a colloidal solution according to Einstein[1] and Hatschek,[2] is given by

$$\eta_v = \eta_o(1+k\varphi) \qquad (3)$$

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[1] Ann. Physik, 19, 289 (1906); 34, 591 (1911).

[2] Kolloid-Z. 7, 310 (1910); 8, 34 (1911).

where φ is the volume-fraction of the disperse phase per unit volume of the solution and k a constant having values 2.5 according to Einstein and 4.5 according to Hatschek. Another formula was empirically derived by Arrhenius[1] for the viscosities of solutions and is represented as

$$\log \eta_v/\eta_o = \theta c \qquad (4)$$

where c is the volume-fraction of the solute per unit volume of the solvent and θ, a constant.

In tables given below φ represents the mass of the solute per unit volume of the solution and is given in column 2. The values of η_v/η_o obtained experimentally are shown in column 3, while those obtained by calculation from Einstein's and Hatschek's formula are given in columns 4 and 5 respectively. The values of θ, a constant referred to the equation (4), are shown in column 6, its value as determined by Arrhenius being 0.01086.

TABLE I

Viscosity of Potassium Palmitate in Ethyl Alcohol at 30°C.

1	2	3	4	5	6
Concentrations	φ	η_v/η_o Obs	η_v/η_o Cal	η_v/η_o Cal	θ
M/30	0.0098 gms	1.0287	1.0245	1.0441	1.255
M/60	0.0049 "	1.0140	1.0122	1.0220	1.225
M/80	0.0036 "	1.0087	1.0090	1.0162	1.028
M/102	0.0029 "	1.0065	1.0072	1.0130	0.931
M/142	0.0021 "	1.0033	1.0052	1.0094	0.667

TABLE II

Viscosity of Potassium Stearate in Ethyl Alcohol at 30°C.

1	2	3	4	5	6
Concentrations	φ	η_v/η_o Obs	η_v/η_o Cal	η_v/η_o Cal	θ
M/30	0.0107 gms	1.0276	1.0267	1.0481	1.103
M/60	0.0053 "	1.0193	1.0134	1.0238	1.547
M/80	0.0040 "	1.0101	1.0100	1.0180	1.075
M/102	0.0031 "	1.0066	1.0079	1.0139	0.903
M/142	0.0023 "	1.0022	1.0056	1.0103	0.435

TABLE III

Viscosity of Potassium Oleate in Ethyl Alcohol at 30°C.

1	2	3	4	5	6
Concentrations	φ	η_v/η_o Obs	η_v/η_o Cal	η_v/η_o Cal	θ
M/30	0.0107 gms	1.0229	1.0267	1.0481	0.925
M/60	0.0053 "	1.0154	1.0132	1.0238	1.246
M/80	0.0040 "	1.0080	1.0100	1.0180	0.850
M/102	0.0031 "	1.0051	1.0077	1.0139	0.677
M/142	0.0022 "	1.0027	1.0055	1.0099	0.545

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[1] Medd. Vetensk. Nobelinstitut. 3, No. 13 (1916).

TABLE IV

Viscosity of Sodium Stearate in Ethyl Alcohol at 30°C.

1 Concentrations	2 φ	3 η_v/η_0 Obs	4 η_v/η_0 Cal	5 η_v/η_0 Cal	6 θ
M/30	0.0102 gms	1.0321	1.0255	1.0459	1.343
M/60	0.0051 "	1.0216	1.0127	1.0229	1.804
M/80	0.0038 "	1.0110	1.0095	1.0171	1.237
M/102	0.0030 "	1.0075	1.0075	1.0135	1.067
M/142	0.0021 "	1.0010	1.0052	1.0094	0.190

TABLE V

Viscosity of Sodium Palmitate in Ethyl Alcohol at 30°C.

1 Concentrations	2 φ	3 η_v/η_0 Obs	4 η_v/η_0 Cal	5 η_v/η_0 Cal	6 θ
M/30	0.0093 gms	1.0210	1.0232	1.0418	0.968
M/60	0.0046 "	1.0121	1.0115	1.0207	1.131
M/80	0.0035 "	1.0076	1.0087	1.0157	0.914
M/102	0.0027 "	1.0061	1.0067	1.0121	0.926
M/142	0.0020 "	1.0025	1.0050	1.0090	0.550

TABLE VI

Viscosity of Potassium Palmitate in n-Butyl Alcohol at 30°C.

1 Concentrations	2 φ	3 η_v/η_0 Obs	4 η_v/η_0 Cal	5 η_v/η_0 Cal	6 θ
M/80	0.0037 gms	1.0257	1.0092	1.0166	2.973
M/90	0.0033 "	1.0204	1.0082	1.0148	2.667
M/100	0.0030 "	1.0160	1.0075	1.0135	2.267
M/120	0.0025 "	1.0117	1.0062	1.0112	2.000
M/160	0.0019 "	1.0064	1.0047	1.0085	1.421

TABLE VII

Viscosity of Potassium Stearate in n-Butyl Alcohol at 30°C.

1 Concentrations	2 φ	3 η_v/η_0 Obs	4 η_v/η_0 Cal	5 η_v/η_0 Cal	6 θ
M/80	0.0040 gms	1.0314	1.0100	1.0180	3.325
M/90	0.0036 "	1.0249	1.0090	1.0162	2.805
M/100	0.0032 "	1.0208	1.0081	1.0144	2.782
M/120	0.0027 "	1.0145	1.0067	1.0121	2.296
M/160	0.0020 "	1.0103	1.0050	1.0090	2.201

TABLE VIII

Viscosity of Potassium Oleate in n-Butyl Alcohol at 30°C.

1 Concentrations	2 φ	3 η_v/η_0 Obs	4 η_v/η_0 Cal	5 η_v/η_0 Cal	6 θ
M/80	0.0040 gms	1.0222	1.0100	1.0180	2.374
M/90	0.0035 "	1.0177	1.0087	1.0157	2.171
M/100	0.0032 "	1.0127	1.0080	1.0140	1.719
M/120	0.0027 "	1.0085	1.0067	1.0121	1.333
M/160	0.0020 "	1.0046	1.0050	1.0090	0.950

TABLE IX

Viscosity of Sodium Stearate in n-Butyl Alcohol at 30°C.

1 Concentrations	2 φ	3 η_v/η_0 Obs	4 η_v/η_0 Cal	5 η_v/η_0 Cal	6 θ
M/80	0.0038 gms	1.0235	1.0095	1.0171	2.658
M/90	0.0034 "	1.0198	1.0085	1.0153	2.500
M/100	0.0030 "	1.0156	1.0075	1.0135	2.200
M/120	0.0025 "	1.0123	1.0062	1.0112	2.081
M/160	0.0019 "	1.0090	1.0047	1.0085	2.000

TABLE X

Viscosity of Sodium Palmitate in n-Butyl Alcohol at 30°C.

1 Concentrations	2 φ	3 η_v/η_0 Obs	4 η_v/η_0 Cal	5 η_v/η_0 Cal	6 θ
M/80	0.0035 gms	1.0184	1.0087	1.0157	2.252
M/90	0.0031 "	1.0168	1.0077	1.0139	2.322
M/100	0.0028 "	1.0142	1.0070	1.0126	2.178
M/120	0.0023 "	1.0120	1.0057	1.0103	2.261
M/160	0.0017 "	1.0073	1.0043	1.0076	1.449

TABLE XI

Viscosity of Potassium Oleate in Iso-Butyl Alcohol at 30°C.

1 Concentrations	2 φ	3 η_v/η_0 Obs	4 η_v/η_0 Cal	5 η_v/η_0 Cal	6 θ
M/80	0.0040 gms	1.0177	1.0100	1.0180	1.900
M/90	0.0035 "	1.0122	1.0087	1.0157	1.515
M/100	0.0032 "	1.0079	1.0080	1.0140	1.063
M/120	0.0027 "	1.0051	1.0067	1.0121	0.778
M/160	0.0020 "	1.0035	1.0050	1.0090	0.750

Discussion of Results

The viscosities of five different soaps have been measured at five dilutions in ethyl, n-butyl and iso-butyl alcohols and the values so obtained have been compared with those calculated from Einstein's and Hatschek's formula. The results indicate that the calculated values (on Einstein's formula) approximate more closely to the observed values at low concentration of the solute. This is in agreement with the theoretical assumptions on which the formula was derived. It will be seen from Tables I-XI that the agreement between the calculated and observed values is more exact at concentrations M/80 and M/102 in solutions in ethyl alcohol and at concentrations M/120 and M/160 in solutions in n-butyl alcohol. The results calculated with K equal to 4.5 (Hatschek's value) are in better agreement with the experimental results in the case of solutions in n-butyl alcohol than in ethyl alcohol.

As will be noted from above tables, the values of the constant calculated from formula (4) are, in all cases examined here, greater than the values found by Arrhenius. Moreover the value of the constant has been found to vary with the nature of the solute and the solvent.

Ethyl alcohol is known to consist of strongly associated molecules in concentrated state which get dissociated on dilution. The results of Horiba[1] of the viscosity of aqueous solutions of ethyl alcohol show that the quotient log η/c_1 decreases with increasing concentration c_1. The same was observed by Baker[2] with solutions of nitrocellulose in acetone. But the results of present investigation show that in almost all cases the Arrhenius constant, that is, quotient $\frac{1}{c}\log \eta_v/\eta_o$ increases with increasing concentration.

Occasionally the solutions were allowed to stand for about a week to observe any change that may take place in the nature of the solutions with time[3]. But in no case any alteration in the time of flow was experienced.

The viscosity correction was applied to the conductivity values according to the formula (1) and the results obtained are shown in Tables XII-XVI. The relation between $\mu_v \eta_v \eta_o$ and V, volume in litres containing one gram-molecule of the solute, still gives a straight line curve between the range of dilutions 30 to 160 litres considered here.

Table XII

Potassium Palmitate

V	Ethyl Alcohol μ_v.	Ethyl Alcohol $\mu_v. \eta_v/\eta_o$.	V	n-Butyl Alcohol μ_v.	n-Butyl Alcohol $\mu_v. \eta_v/\eta_o$.
30	27.59	28.38	80	4.552	4.669
60	30.81	31.24	90	4.967	5.069
80	33.33	33.61	100	5.135	5.216
102	37.53	37.76	120	5.759	5.826
142	42.36	42.49	160	6.665	6.707

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[1] J. Tokio Chem. Soc. 31, 922 (1910).

[2] J. Chem. Soc. 108, 1653 (1913).

[3] Cf. Dunstan and Thole: "Viscosity of Liquids", p. 65 (1914).

TABLE XIII

Potassium Stearate

V.	Ethyl Alcohol		V.	n-Butyl Alcohol	
	μ_v.	$\mu_v.\eta_v/\eta_0$		μ_v.	$\mu_v.\eta_v/\eta_0$.
30	31.54	32.41	80	5.386	5.555
60	42.46	43.27	90	5.399	5.533
80	43.07	43.50	100	5.520	5.633
102	47.90	48.19	120	6.308	6.397
142	58.05	58.19	160	8.028	8.110

TABLE XIV

Potassium Oleate

V.	Ethyl Alcohol		V.	n-Butyl Alcohol	
	μ_v.	$\mu_v.\eta_v/\eta_0$		μ_v.	$\mu_v.\eta_v/\eta_0$
30	22.22	22.74	80	4.307	4.403
60	28.80	29.24	90	4.620	4.701
80	32.71	32.96	100	4.906	4.968
102	36.92	37.10	120	5.520	5.585
142	46.10	46.23	160	6.540	6.569

TABLE XV

Sodium Stearate

V.	Ethyl Alcohol		V.	n-Butyl Alcohol	
	μ_v.	$\mu_v.\eta_v/\eta_0$		μ_v	$\mu_v.\eta_v/\eta_0$.
30	25.87	26.70	80	4.206	4.304
60	30.81	31.47	90	4.319	4.404
80	36.80	37.19	100	4.329	4.395
102	38.17	38.45	120	4.999	5.060
142	43.54	43.58	160	6.422	6.477

TABLE XVI

Sodium Palmitate

V.	Ethyl Alcohol		V.	n-Butyl Alcohol	
	μ_v	$\mu_v.\eta_v/\eta_0$		μ_v	$\mu_v.\eta_v/\eta_0$
30	21.22	21.66	80	3.924	3.996
60	30.11	30.47	90	4.227	4.297
80	——	——	100	4.505	4.568
102	36.32	36.53	120	4.906	4.966
142	43.54	43.65	160	5.987	6.030

The degree of dissociation could not be determined owing to want of the values of μ_α which, as the work of Mahin, Kreider and others has shown, occurs generally at dilution of 50,000 liters and for the measurement of which the Kohlrausch bridge with ordinary buzzer and telephone is unsuitable. More work on this line will be done over a large range of dilutions to collect sufficient data to calculate the degree of dissociation at each concentration and then to examine more precisely the behaviour of soap solutions in non-aqueous solvents.

The author takes this opportunity of thanking Dr. S. S. Bhatnagar for his valuable suggestions and keen interest shown throughout the whole investigation.

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THE DETECTION OF CONSTANT-BOILING MIXTURES

BY T. R. BRIGGS

Professor Orndorff has called my attention to the apparent lack of any simple laboratory method of distinguishing[1] an azeotropic[2] mixture from a chemical individual, since both boil at constant temperature, and thus may be distilled without change. The following experiments were therefore undertaken to supply such a method and were carried out and confirmed independently by several of my students during the course of their undergraduate research. Elaborate apparatus was avoided purposely, so that no great degree of exactness can be claimed for the results. The principle underlying the method is well known; but since the experiments are instructive and well fitted, by reason of their simplicity, to be included in a laboratory course in physical chemistry, they are deemed worth describing.

It has long been recognized that the composition of a constant-boiling mixture varies with the pressure under which the process of ebullition is carried out. Thus it is known that a decrease in pressure displaces the composition of the azeotropic mixture toward the acid side in the case of hydrochloric acid and water, and toward the alcohol side in the case of ethyl alcohol and water[3]. It is evident, therefore, that a mixture which is azeotropic at one pressure will not be azeotropic at some other pressure, and will change in composition if distilled at this pressure. The extent to which this change in composition takes places will depend upon the effectiveness of the still-head, the slope of the temperature-composition curves in the neighborhood of the azeotropic points and the magnitude of the displacement which the pressure change produces. Such, in brief, is the principle on which these experiments are based.

Two general cases arise (1) where the azeotropic boiling point is a maximum, (2) where the azeotropic boiling point is a minimum, and as examples of these I have chosen the systems, hydrochloric acid-water and methyl alcohol-benzene, respectively. The azeotropic mixture (A_o) in each of these systems, prepared at atmospheric pressure (P_o) has been distilled at a lower pressure (P_1) through a fractionating column, and the changes in composition which have resulted have been noted by direct analysis or by observing some physical property, such as the density.

The exact nature of these changes may best be understood by considering the temperature-composition diagrams for the two systems in the neighborhood of the azeotropic points. These diagrams have been sketched in Fig. 1, in which no attempt has been made to draw the curves to scale. The lines

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[1] Cf. Forster and Withers: J. Chem. Soc., 99, 266 (1911).

[2] Cf. Young: "Distillation Principles and Processes", 46 (1922); Wade and Merriman: J. Chem. Soc., 99, 1004 (1911).

[3] Wade and Merriman: J. Chem. Soc., 99, 997 (1911); Merriman: Ibid., 103, 628 (1913).

marked V_0 and V_1, R_0 and R_1, represent the compositions of vapor and liquid respectively at the pressures P_0 and P_1, A_0 and A_1 being the corresponding azeotropic compositions.

In the case of hydrochloric acid and water the constant boiling mixture A_0, prepared by distillation at P_0, will begin to boil under the pressure P_1 at a temperature represented by the point *b* and the vapor will have the composition denoted by *b'*. On distilling A_0 with a fractionating column, the distillate will therefore contain relatively less of the acid and more of the water, and if distillation be continued, the residue in the flask will attain the composition represented by *c*, and will be transformed into the low pressure azeotropic mixture A_1. When this point has been reached, no further change in composition is possible so long as the pressure remains constant. Since the density of solutions of hydrochloric acid is greater than that of water, the density of the first portions of distillate will be less than that of the residue, while the density of the latter will rise, until at length it equals that of the new constant boiling mixture. Progressive changes in density such as these, since they could not possibly occur with a single chemical individual, serve to differentiate clearly between the latter and a mixture of constant boiling point.

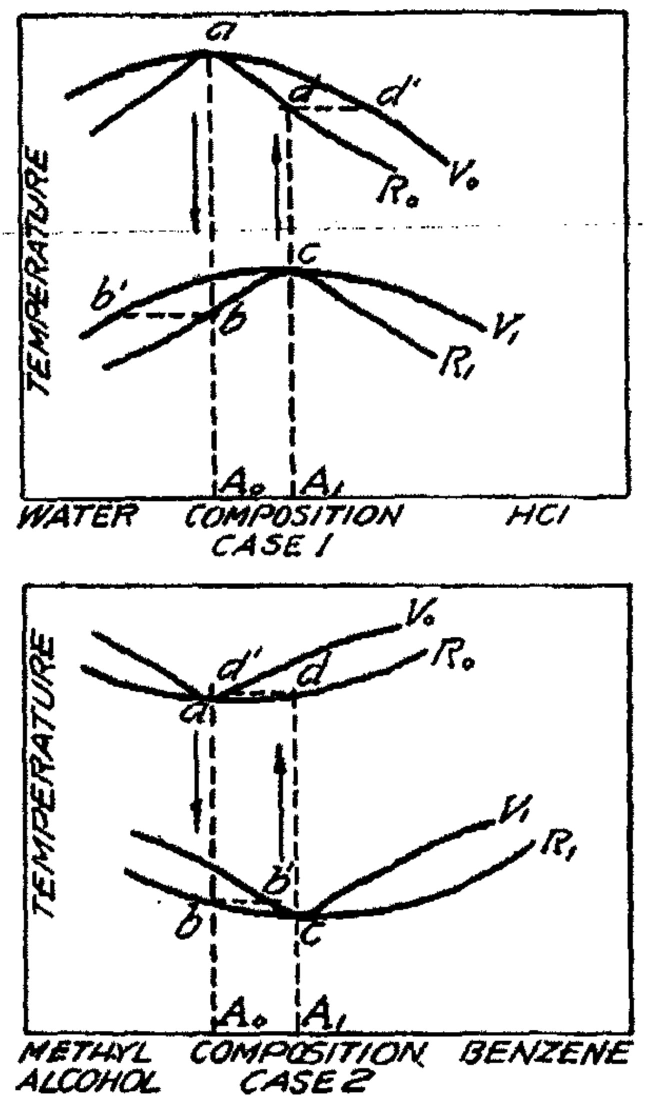

Fig. 1

The conclusions formulated in the preceding paragraph were then subjected to experimental proof. A liter of the azeotropic mixture A_0 of hydrochloric acid and water was prepared at atmospheric pressure by making a 20.2 percent solution of the acid and distilling until distillate and residue had the same composition—as determined by titration with standard sodium hydroxide—and the same density, as ascertained with a Westphal balance. This azeotropic mixture was then fractionated at a pressure of about 50 mm, and the average composition of an unspecified volume of the distillate was compared at regular intervals with the composition of the residue remaining in the flask, care being taken to collect the distillate in a filter flask immersed in ice. Since the pressure fluctuated a good deal no attempt was made to measure the temperature of distillation. The data follow.

TABLE I

Hydrochloric Acid and Water

Fractionation of the Azeotropic Mixture under Diminished Pressure.

	Pressure mm	Specific Gravity		Grams HCl per cc	
		Distillate	Residue	Distillate	Residue
Azeotropic Mixture A_0	750	1.101	1.101	0.222	0.222
	50	1.035	1.103	0.074	0.227
	"	1.044	1.104	0.094	0.229
	"	1.060	1.108	0.130	0.238
	"	1.075	1.110	0.164	0.243
	"	1.092	1.112	0.201	0.248
	"	1.103	1.113	0.226	0.250
	"	1.105	1.113	0.232	0.251
Azeotropic	"	1.112	1.114	0.249	0.252
Mixture A_1	"	1.114	1.114	0.252	0.252

These data confirm the theory in an entirely satisfactory manner. It will be observed that the first sample of distillate collected at 50 mm contains only about 7 percent of hydrochloric acid compared with 20.2 percent in the original solution and that the low-pressure azeotropic mixture ultimately formed contains about 22.6 percent and gives rise to a distillate of equal density and composition.

If we turn our attention a second time to the temperature-composition diagram, it will be seen that if the low-pressure azeotropic solution A_1 (the residue from the preceding run) be distilled at the *original* atmospheric pressure P_0, fractionation again becomes possible. The mixture will begin to boil at *d*, and since the composition of the vapor at the same temperature is represented by *d'* the distillate on fractionation will contain more hydrochloric acid than the residue in the flask. The latter will accordingly become more dilute as distillation continues, until at length the composition attains the point *a* and the original constant-boiling mixture A_0 is reproduced. This process, constituting the *reverse* of the distillation at 50 mm, was tested experimentally with the following results.

It will be observed that distillation gave the expected results. The first sample of distillate is an almost saturated solution of hydrochloric acid gas in water at atmospheric pressure and the final constant-boiling mixture is identical with the one with which these experiments were started (Cf. Table I). Regarding the two distillations as a whole, it will be seen that the residue in the flask has been caused to change through a complete cycle, which may be represented in the diagram of Fig. 1 by the closed path *abcda*. No cyclic process of this nature can possibly be carried out with a liquid which consists of a single chemical individual.

TABLE II

Hydrochloric Acid and Water

Fractionation of the Low-Pressure Azeotropic Mixture at Atmospheric Pressure

	Pressure mm	Specific Gravity		Grams HCl per cc	
		Distillate	Residue	Distillate	Residue
Azeotropic Mixture A_1	50	1.114	1.114	0.252	0.252
	750	1.198	1.110	0.464	0.243
	"	1.144	——	0.325	——
	"	1.124	——	0.275	——
	"	1.114	——	0.253	——
	"	1.110	——	0.242	——
	"	1.105	——	0.233	——
	"	1.103	——	0.228	——
	"	1.102	——	0.225	——
Azeotropic Mixture A_0	"	1.101	——	0.223	——
	"	1.101	——	0.223	0.222

The system methyl alcohol and benzene was next studied as an example of the second general case where the boiling point of the azeotropic solution is a minimum. The pressure-composition diagram has been sketched in Fig. 1. Consideration of this diagram shows that the azeotropic mixture A_0, on being fractionated at diminished pressure P_1, gives rise to a *distillate*, the composition of which is practically that of the point *c* and which constitutes the low pressure azeotropic mixture A_1. While this distillate is being formed, the residue in the flask must necessarily grow richer in alcohol. Changes occur in composition, and therefore in density, and these are sufficient to distinguish the original mixture from a chemical individual.

Methyl alcohol was purified by the method recommended by Duclaux and Lanzenberg[1]. The boiling point was found to be 66.5°. The alcohol was then mixed with redistilled benzene to give a solution containing about 60 percent by weight of the latter and the whole fractionated at atmospheric pressure. The distillate thus obtained was found to be the azeotropic mixture A_0, as was shown by a separate fractionation in the course of which no difference in density was observed between distillate and residue. This constant-boiling mixture was then fractionated under a pressure of about 158 mm, with the following results:—

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[1] Bull., 29, 35 (1921).

TABLE III

Methyl Alcohol and Benzene

Fractionation of the Azeotropic Mixture under Diminished Pressure

	Pressure mm	Specific Gravity	
		Distillate	Residue
Azeotropic Mixture A_0	734	0.849	0.850
	157	0.855	0.850
	157	0.854	0.850
	159	0.854	0.849
	158	0.855	0.848
	157	0.854	0.845
		Azeotropic Mixture A_1	

The specific gravity of benzene is 0.879, compared with 0.790 for alcohol. It is evident, therefore, that the residue contains more alcohol as the distillation progresses while the distillate remains constant in composition and contains more benzene than the original constant-boiling mixture. Had the distillation been carried far enough so that only a small amount of residue remained, the distillate at length would have shown an increase in alcohol content. Actually the distillation was brought to a close before this change had time to begin, but was continued until a sufficient volume of the azeotropic mixture A_1 was made available for the remainder of the work. The low-pressure constant-boiling mixture is relatively richer in benzene. Just as in the preceding case of hydrochloric acid and water, the changes in density during fractionation serve to distinguish the constant-boiling mixture from a single chemical individual.

To prove that the distillate obtained under diminished pressure was actually the azeotropic mixture, it was fractionated under the same pressure. No changes in density occurred, as the following data show.

TABLE IV

Methyl Alcohol and Benzene

Fractionation of the Low-Pressure Azeotropic Mixture under Diminished Pressure

Pressure mm	Specific Gravity	
	Distillate	Residue
157	0.855	0.855
159	0.855	0.855

Fractionation of the low-pressure constant-boiling mixture was then carried out at atmospheric pressure, to complete the cycle. The results follow.

TABLE V

Methyl Alcohol and Benzene

Fractionation of the Low-Pressure Azeotropic Mixture under Atmospheric Pressure

	Pressure mm	Specific Gravity	
		Distillate	Residue
Azeotropic Mixture A_1	740	0.849	0.855
	"	0.849	0.856
	"	0.849	0.858
	"	0.849	0.864
		Azeotropic Mixture A_0	

By referring to the temperature-composition diagram it is apparent that fractionation of the low-pressure azeotropic mixture A_1 at atmospheric pressure P_0 will give rise to a distillate of which the composition is represented very closely by the point *a* and which is therefore identical with the original constant boiling solution A_0. The residue, on the other hand, will increase in benzene content as the distillate is produced, until at length the composition of the distillate will also begin to change toward the benzene side. In the last experiment the fractionation was not carried far enough to give rise to a progressive change in the distillate, but it may be seen that the distillate is identical with the azeotropic mixture A_0 while the residue is growing slowly richer in benzene. Taken as a whole, the experiments with methyl alcohol and benzene represent a complete cycle, in which the composition of the *distillate* has traced the path *abcda*, whereas this path was followed by the *residue* in the case of hydrochloric acid and water.

In distinguishing between a constant-boiling mixture and a pure liquid, completion of the whole cycle is of course unnecessary. A single fractional distillation at low pressure will ordinarily suffice. If there is a difference in density between the residue and the first sample of distillate the liquid under test is a mixture, even though it can not be distinguished from a chemical individual when boiled at atmospheric pressure. It should be noted, however, that there is one case where the test will fail, for if the two constituents in the mixture are dynamic isomers between which equilibrium is reached practically instantaneously, the mixture will behave as a single individual at all pressures and no changes during distillation will be possible.

The detection of constant-boiling mixtures could be carried out by applying the same general theory in a different way. The azeotropic mixture obtained at atmospheric pressure, instead of being distilled under diminished pressure, could be distilled at atmospheric pressure in a current of air. The latter would serve to lower the partial pressures of both water and acid in the vapor, and the effect would be virtually the same as if the constant boiling mixture were being distilled under diminished pressure. Fractionation would therefore take place, and would serve to distinguish the original mixture from a pure liquid. This method was not tested by actual experiment, but a third possible method, as described in the next paragraph, was tried instead.

If a thermometer be placed in the vapor just above the liquid in the distilling flask and a second thermometer in the escaping vapor at the top of the fractionating column, there will be no difference in theory between the readings on the two instruments if fractionation is not occurring and the pressure is the same in two places. There will thus be little or no difference between the thermometer readings whether the liquid being distilled is a chemical individual or an azeotropic mixture. In the latter case, however, a change of pressure will cause fractionation to begin, as we have seen, and the upper thermometer as a result should read noticeably less than the lower one. This method was tried out experimentally, but while the data obtained from the thermometer readings were more or less in agreement with the preceding statement, it proved so difficult to keep from superheating the vapor in the flask, and to maintain the pressure constant during the low pressure distillation, that the method was abandoned. It could no doubt be made to work if all the necessary precautions were taken, at least for those cases where there is a sufficient difference between the boiling point of the azeotropic mixture and the boiling points of the pure components.

Summary

1. A simple laboratory method for distinguishing between a chemical individual and an azeotropic or constant-boiling mixture has been described.

2. The method is based on the familiar principle that a change of pressure displaces the azeotropic composition.

3. The method has been applied experimentally to the two systems: hydrochloric acid-water, and methyl alcohol-benzene.

4. In each of these systems, a complete distillation cycle, reversible in respect of either the residue or the distillate has been demonstrated by experiment.

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ADSORPTION FROM SALT SOLUTIONS BY COLLOIDAL COPPER FERROCYANIDE[1]

BY MIKKEL FRANKERT AND JOHN A. WILKINSON

Introduction

The water extract from a soil may be acid due to the presence of soluble organic or inorganic acids, or to acid set free by the hydrolysis of salts of aluminium or iron. In addition to this, however, some acid may be developed when the soil is treated with a solution of a neutral salt such as KNO_3. There are two explanations given as to the cause of this latter acidity.

In one, the acidity is said to be due to the presence in the soil of insoluble silicic acids which on treatment with the salt solution exchange the acid H for an equivalent amount of the metal ion of the salt and thus set free in the solution an equivalent amount of acid. This view is usually called the base exchange theory[2].

In the other, the acidity is said to be due to the selective adsorption of the hydroxyl ion from the water and the metal ion from the salt by the soil particles, especially the colloidal fraction, thus leaving an equivalent amount of acid in the solution. This is designated as the adsorption theory[3]. The purpose of this investigation was to use a colloidal material of known composition and one capable of base exchange and treat this with salt solutions in an endeavor to find if any acidity was developed, if any base exchange took place, and if there was any relationship between the base exchange and the acidity developed. For this purpose colloidal copper ferrocyanide was chosen because it is easily prepared pure and very small amounts of copper may be accurately determined to show whether or not any base exchange has taken place.

Preparation of Materials

A large amount of copper ferrocyanide was prepared by rapidly mixing solutions containing equivalent amounts of copper chloride and potassium ferrocyanide. The precipitate was washed with distilled water by decantation until peptization became quite marked, was then filtered, dried on a hot plate at 50°C[4], ground in a mortar and again washed by decantation until peptization began. The wash water then showed no test for chlorides. The solid was dried as before and ground to pass a 120-mesh sieve. Sufficient copper ferrocyanide was made at one time for all the experiments.

When this copper ferrocyanide was suspended in distilled water in a U tube with a difference of potential of 110 volts across the arms, the particles moved to the anode showing that they were negatively charged.

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[1] Contribution from Chemical Laboratory Iowa State College.

[2] Truog: J. Phys. Chem. **20**, 457 (1916). Truog calls this acidity mineral acid.

[3] Bancroft: Applied Colloid Chemistry, p. 120; Harris: J. Phys: Chem. **18**, 355 (1914); Cameron: **14**, 400 (1910).

[4] Care must be taken not to heat copper ferrocyanide much above 50° as it will take fire spontaneously.

The solutions were all made with conductivity water and with the exception of the HCl, KOH, and aluminium salts were all made neutral to phenolphthalein, by using the corresponding base or acid, before adding them to the copper ferrocyanide. After equilibrium was reached, the solutions were brought to the same end-point in determining the acidity developed. In the case of the aluminium salts, alizarin yellow was used in place of phenolphthalein as the color of the former indicator is not affected by the hydrolysis of the aluminum salts.

Procedure

A. *Determination of the Acidity or Alkalinity developed.*

The amount of acidity or alkalinity developed was determined by placing two grams of the colloidal copper ferrocyanide in each of a series of 150 cc flasks and adding varying quantities of water and salt solution to them. Sufficient water was added in each case to make the total volume of solution 75 cc. The figures on the graphs are the number of cc of the salt solution present in 75 cc of the solution added to two grams of copper ferrocyanide. The concentration of the solution was usually normal unless the solubility of the salt was lower than this. In all cases the concentration is indicated on the graph. It was found that eight hours was a sufficient length of time for the system to come to equilibrium if the contents were shaken occasionally. However the flasks were always allowed to stand at least forty eight hours to insure equilibrium.

At the end of the adsorption period twenty five cc of the supernatant liquid, if clear, was pipetted off and titrated to the same end-point as had been used before adding to the copper ferrocyanide. If the liquid was not clear it was centrifuged at a speed of 1500 r.p.m. until it cleared, which required several hours in some cases. If, as happened in a few cases, this did not clear the solution, a few drops of KCl solution were added, which caused the colloid to settle immediately on centrifuging. Since the amount of acid or base developed was sometimes very small, it was necessary to duplicate exactly the color change of the indicator. The titrations were therefore made in 50 cc Nessler tubes, and were usually made with a 0.01 N solution unless the acidity or alkalinity developed became large and then more concentrated solutions were used and the results calculated and expressed in terms of 0.01 N. Only when much copper was dissolved was any difficulty experienced in getting an end-point the same as the original.

B. *Determination of the Amount of Copper dissolved.*

The copper was determined colorimetrically, the standard set being made from a solution of copper sulphate containing 0.1 gram of copper per liter. The standards contained from 1 to 10 cc of this solution and 2 cc of concentrated ammonium hydroxide and were diluted to 50 cc in Nessler tubes. In determining the amount of copper dissolved, any colloidal copper ferrocyanide was precipitated and filtered out and 25 cc of the filtrate was treated with 2 cc of concentrated ammonium hydroxide, diluted to 50 cc in a Nessler tube and compared with the standard set. In case the ammonium hydroxide formed a precipitate, as it did with the aluminum and barium salts, this was filtered out before diluting in the Nessler tube. If the copper content was more than 0.001 gram an aliquot part was taken for comparison. An amount of copper less than 0.0001 gram in 25 cc could not be determined by this method and since 25 cc was taken for analysis from the 75 cc of the liquid above the copper ferrocyanide the minimum amount of copper reported is 0.0003 gram.

Data

The results obtained are shown in Figs. 1, 2, 3, and 5. In the first three the concentration of the salt solution, expressed as cc of N solution present in 75 cc of solution, is plotted against the cc of 0.01 N acid or base that was devel- oped in the 75 cc of solution after coming to equilibrium in contact with two grams of the copper ferrocyanide. In Fig. 5 the amount of copper found in 75 cc of the solution is plotted against the concentration of the salt solution.

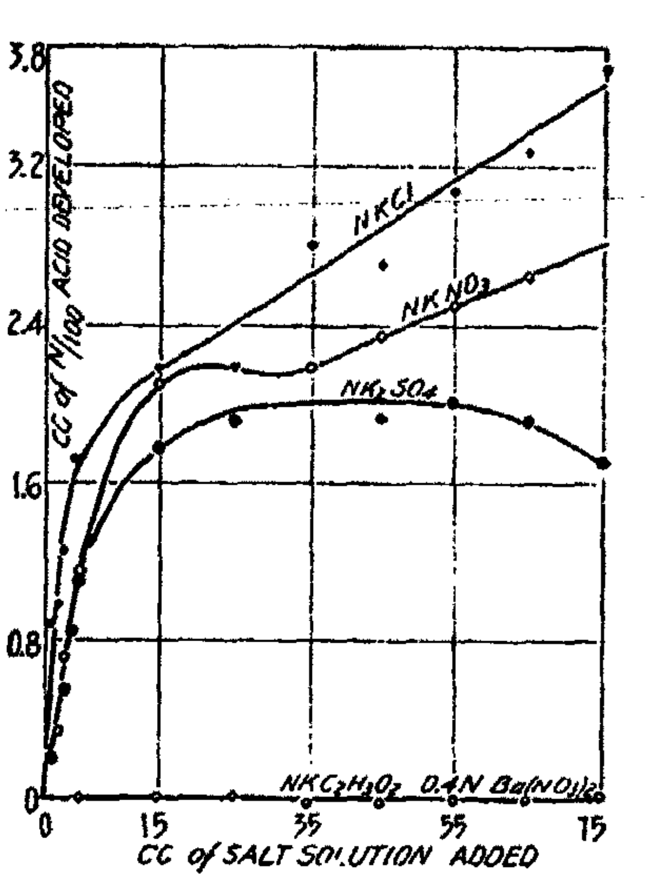

FIG. 1

Discussion of Data

The potassium salts, Fig. 1, show a gradual change from developing a small amount of acidity with the chloride to large amounts of alkalinity with the ferrocyanide. The acetate gives a neutral solution at all concentrations of the salt while the ferrocyanide develops alkalinity first and then changes to acid up to 1.2 cc of 0.01 N and beyond that becomes less and less acid approaching neutrality. Dipotassium hydrogen phosphate and potassium ferrocyanide both develop alkalinity the latter being much the larger in amount.

It is difficult to see how any acidity or alkalinity can be developed by the replacement of the copper of copper ferrocyanide by potassium from potassium salts, especially from potassium ferrocyanide, on the basis of base exchange. On the principle of selective adsorption the explanation is that in water the copper ferrocyanide adsorbs the OH^- ion more than H^+ and becomes negatively charged as is indicated by the cataphoresis which was mentioned before. On the addition of KCl both ions are adsorbed but the K^+ ion in the larger amount being sufficient to neutralize both the Cl^- and OH^-. The colloid is precipitated, carrying down with it the adsorbed ions, with the result that there is left in solution an amount of HCl equivalent to the OH^- adsorbed or it may be considered as equivalent to the excess of K^+ ion adsorbed over the Cl^- ion.

With the nitrate the same thing occurs with the exception that the nitrate ion is more adsorbed than the Cl^- ion and so less OH^- ion can be taken up. As a result less acid will be set free by the K^+ ion neutralizing OH^-. That is, the more of other negative ions that are taken up the less OH^- can be held. That this is the explanation is supported by the fact that $SO_4^=$ ion is more effective in cutting down the acidity than is the NO_3^- and it is known that in general it is more adsorbed by a negative colloid than is the NO_3^-. The order of the adsorption of anions from solution by copper ferrocyanide as shown by the acidity developed is $Cl^- < NO_3^- < SO_4^= < Fe(CN)6^{\equiv} < OH^-$ and Acetate$^-$ $< HPO_4^= < Fe(CN)_6.^{==}$

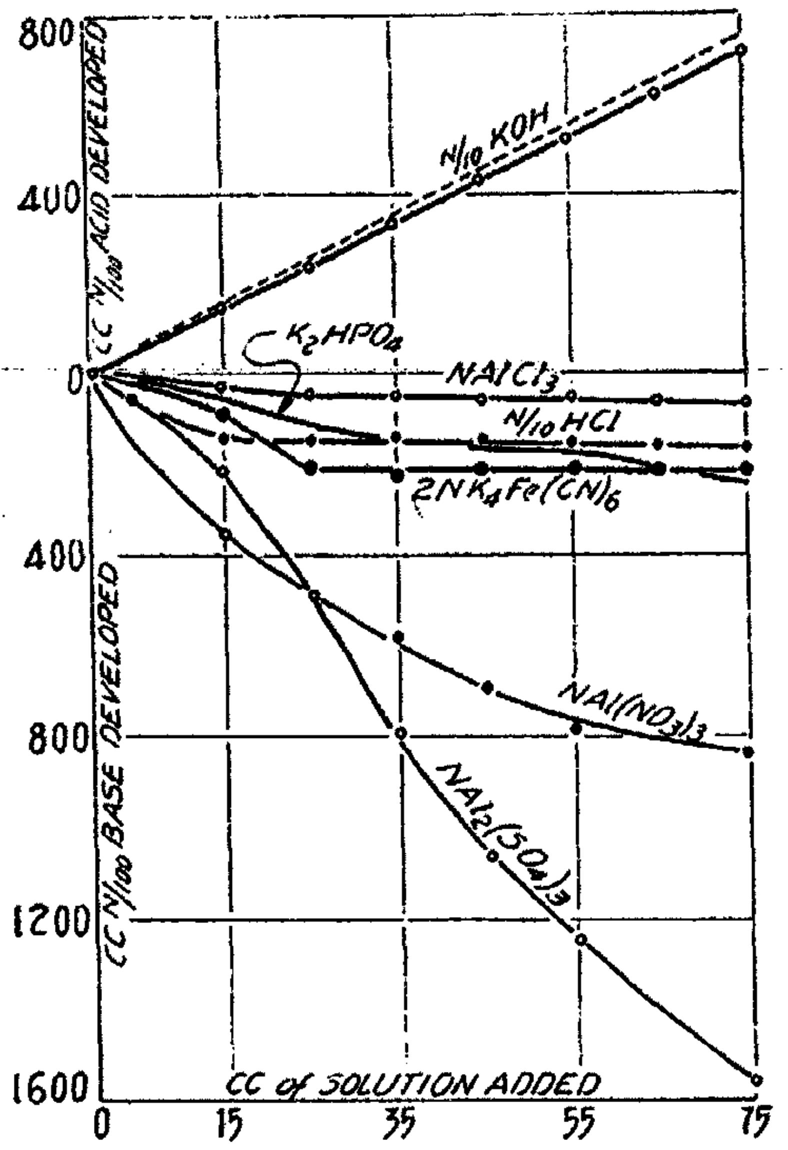

FIG. 2

In the last two cases they are so highly adsorbed that they overcome completely the effect of the adsorption of the K^+ and OH^- ions and cause the colloid to adsorb some of the H^+ ions from the water with the result that the solution becomes alkaline and, in the case of the ferrocyanide, this amounts to 200 cc of 0.01 N KOH solution. The ferrocyanide being the anion of the colloid and having the high negative valence is highly adsorbed.

With the ferricyanide, Fig. 3, the solution is first alkaline due to the adsorption of $Fe(CN)_6^{\equiv}$ and H^+ ions, leaving an equivalent amount of KOH in solution. Soon however the K^+ ion becomes effective and cuts down the alkalinity due to the $Fe(CN)_6^{\equiv}$ and finally overcomes it entirely and the solution becomes acid. These results are plain if the forms of the adsorption curves are assumed to be as shown in Fig. 4.

The experimental curve will be the resultant or the difference between the two because one of them tends to develop acid and the other base. At first the adsorption of the $Fe(CN)_6^{\equiv}$ is greater than K^+ and the difference increases up to the point A and this represents the point of greatest alkalinity. From there the difference decreases to the point B where the two ions are equally adsorbed and the solution is neutral. Beyond B up to the point C the adsorption of the K^+ is the greater and the difference increases up to the point C which is the point of maximum acidity. Beyond C the difference gets less and less and the acidity falls off proportionally. The curve for the ferricyanide is interesting since it indicates that each ion has its own adsorption curve and the experimental curve that is obtained is the resultant of all the separate curves.

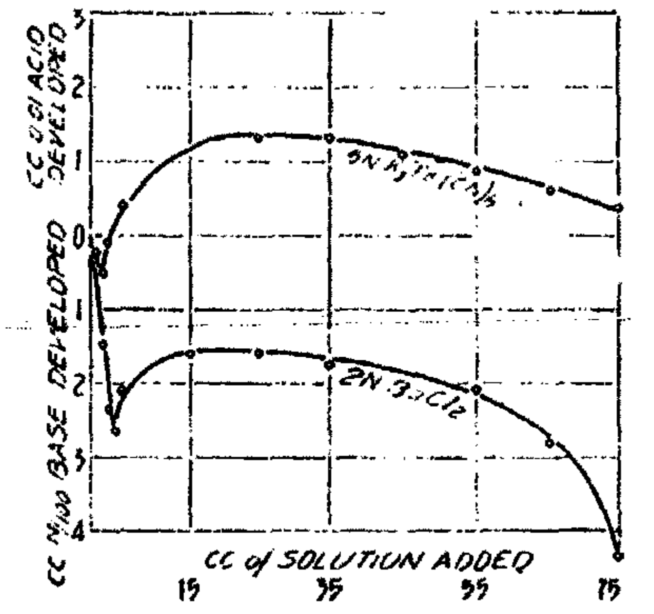

FIG. 3

The curve for KOH, Fig. 2, shows the strong adsorption of the base when present alone. The dotted line shows the amount of KOH added and the full line the amount taken up. The two lines coincide until the concentration is 5 cc of 0.1 N KOH in 75 cc of solution and beyond that they are close together until at 75 cc of 0.1 N solution the copper ferrocyanide adsorbs 95% of the KOH. In dilute solutions of KOH the colloid is very highly peptized.

The curve for HCl shows that it is completely removed up to 10 cc of 0.1 N HCl 75 cc of solution but the percent adsorbed beyond that point decreases very rapidly and from a 0.1 N solution only 21.3% is taken up. This shows the less tendency to adsorb the H^+ ion than the OH^-. It is to be noted that although HCl alone is completely adsorbed up to 10 cc of 0.1 N in 75 cc, in the presence of KCl the equilibrium is reached with less than 3 cc of 0.01 N acid present. This may mean either that the KCl has saturated the colloid so that it cannot take on as much HCl or that more acid had been formed with KCl but had been taken up.

The aluminium salts all develop alkalinity and the order is the same as for the potassium salts, namely $Cl < NO_3 < SO_4$. This might be looked upon as being due to the hydrolysis of the aluminium salts and the adsorption of the free acids. The curve for the $AlCl_3$ follows in the neighborhood of that for HCl.

However one would not expect $Al(NO_3)_3$ to be so much more hydrolyzed than is $AlCl_3$. It seems better to consider that colloidal copper ferrocyanide tends to adsorb negative ions and the more positive they are (the less negative) the less they will be adsorbed. The trivalent aluminium ion will be less adsorbed than the monovalent potassium and therefore the solution will tend to be less acid (more basic) with Al^{+++} than with K^+.

That this is the better explanation is shown by the fact that $Ba(NO_3)_2$ and potassium acetate curves are alike. The solutions develop neither acid or alkali. With the nitrates divalent Ba^{++} being intermediate between trivalent Al^{+++} and monovalent K^+ the curve falls between them. The acetate ion adsorption is equivalent to the monovalent K^+ while the NO_3^- which is less adsorbed than the acetate is equivalent to the Ba^{++} ion which is less adsorbed than the K^+. The hydrolysis of $Ba(NO_3)_2$ would not be of sufficient amount to account for the difference between it and KNO_3. Further $Ba(NO_3)_2$ and $KC_2H_3O_2$ which give identical curves for adsorption are certainly not of the same order of hydrolysis.

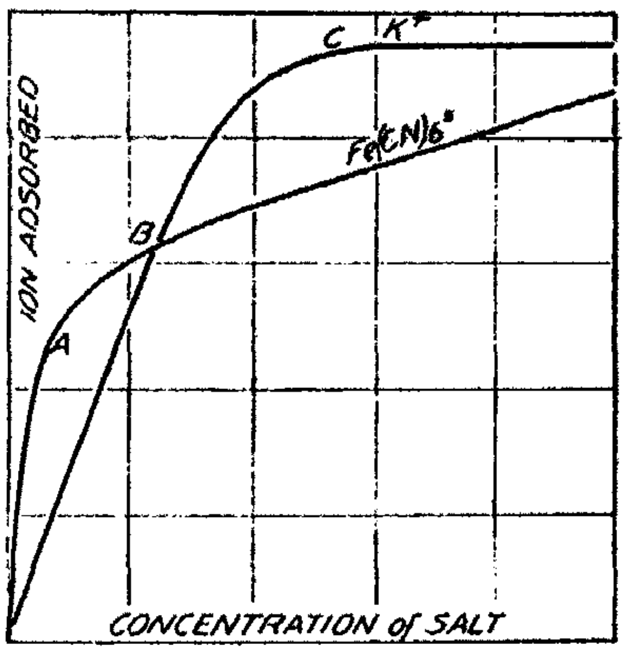

Fig. 4

The curve for $BaCl_2$, Fig. 3, is of the same type as that of $K_3Fe(CN)_6$ as it develops alkalinity first, becomes less alkaline and finally more alkaline again. The explanation is the same as the ferricyanide, the divalent Ba^{++} is less effective than the monovalent Cl^- at first but soon tends to overcome it just as the monovalent K^+ overcame the trivalent Fe(CN$_6^{\equiv}$. In this case however the Ba^{++} is never entirely able to overcome the Cl^- and so the solution never becomes acid or even neutral.

An examination of Fig. 5 showing the amounts of copper dissolved brings out the following points: (a) HCl which was completely adsorbed up to 10 cc of 0.1 N in 75 cc of solution shows no copper up to that point and beyond that point the increase in copper is regular until in the 0.1 N solution 0.038 gram of copper has dissolved. The copper equivalent to the HCl lost from the solution would be $75 \times 0.213 \times 0.03175 = 0.0507$ grams. This shows that the amount of copper dissolved is not equivalent to the acid lost. It seems therefore that adsorption takes place first and this is followed by chemical action.

(b) With KOH (the data are not shown) the copper ferrocyanide was highly peptized especially in the dilute solutions but no test for dissolved copper was obtained as it was probably precipitated as the hydroxide. Only at higher concentrations could a test for $Fe(CN)_6^{\equiv}$ be obtained, the first trace being shown at 15 cc of 0.1 N KOH in 75 cc of solution. This indicates that some chemical action had taken place.

(c) KCl which gave the most acidity showed no copper in solution and the same is true for the nitrate which showed the next amount of acidity. The sulphate gave a mere trace of copper at 40 cc of N solution in 75 cc. After the sulphate the K_2HPO_4 which developed alkalinity gave the most copper in solution. The order of the effect of the anions on the copper dissolved is as follows: (Cl and NO_3 have no effect) $< SO_4 < HPO_4 <$ acetate. This is nearly the reverse of the order of development of acidity with the exception of the acetate. The ferrocyanide and the ferricyanide leave no copper in solution because of the excess of the ferro and ferricyanide ions which would precipitate any copper ions that dissolved.

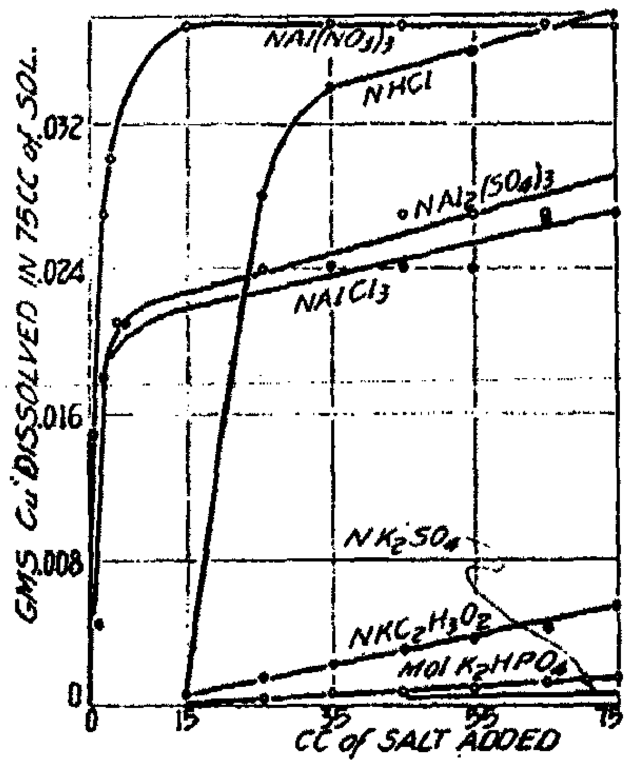

Fig. 5

(d) With the aluminium salts the order is different from the order with potassium. The amounts of copper dissolved are in the following order: $NO_3 > SO_4 > Cl$. The latter two being about equal amount while the former is considerably greater. This might be considered to be due to the oxidizing effect of the nitrate but if this were the explanation the curve for the copper dissolved would show more of a proportionality between the concentration of the salt and the copper dissolved. Instead of that it rises very rapidly and reaches almost a constant value. That it is not due to the nitrate is shown by the fact that neither KNO_3 or $Ba(NO_3)_2$ show any copper dissolved at any concentrations. There is no relationship either direct or indirect between alkalinity developed and the copper dissolved by aluminum salts. If we take the values for 75 cc of N salt solution in 75 cc of solution we get the following table:

	cc 0.01 N alkali dev.	gm copper dis.
$AlCl_3$	60	0.0270
$Al_2(SO_4)_3$	1425	0.0290
$Al(NO_3)_3$	815	0.0375

Conclusion

(1) The acidity and alkalinity developed by the treatment of colloidal copper ferrocyanide with different salt solutions have been determined.

(2) The amounts of copper set free in these same solutions have been determined.

(3) The colloidal copper ferrocyanide has been shown to develop a complete series from slight acidity to stronger alkalinity depending on the nature of the anions and cations used.

(4) The forms of the acidity curves are best explained by selective adsorption. This is best shown in the case of $K_3Fe(CN)_6$ which first developed alkalinity and then acidity.

(5) With HCl adsorption precedes chemical action and is complete up to 10 cc 0.1 N HCl in 75 cc of solution.

(6) With KOH adsorption is complete up to a concentration of 15 cc of 0.1 N in 75 cc of solution and beyond that point up to a 0.1 N solution it is always more than 95% complete.

(7) With the potassium salts the amount of copper dissolved is in an inverse order to the amount of acidity developed. The acetate is an exception to this.

(8) With aluminium salts there is no definite relationship between the amounts of copper dissolved and the alkalinity developed.

(9) The results are explained better on the basis of the adsorption theory rather than that of base exchange.

Ames, Iowa
March, 1924.

REFRACTIVITY AND THE MOLECULAR PHASE HYPOTHESIS. I.

BY E. C. C. BALY AND R. A. MORTON

It is well known that the Sellmeyer dispersion formula in its simplest form expresses the refractivity of substances with considerable accuracy, provided that the characteristic absorption frequency lies in the extreme ultra-violet region of the spectrum. This has been clearly shown by Mr. and Mrs. Cuthbertson in the case of many gaseous elements and compounds.[1] The formula is usually written in the form

$$n^2 - 1 = \frac{N}{\nu_0^2 - \nu^2}$$

where n is the refractive index for light of the frequency ν, N is a constant and ν_0 is the characteristic frequency in the ultra-violet. In the case of gases where the indices are not much greater than unity, n−1 may be used in place of n^2-1.

This formula does not apply at all well if the substance exhibits an absorption band in the near ultra-violet as well as in the extreme ultra-violet. This is particularly noticeable with ozone and the halogen elements, all of which exhibit absorption bands in the long-wave ultra-violet. In Table I are given the observed refractivities of chlorine together with the values calculated from the formula

$$n - 1 = \frac{7.3131 \times 10^{27}}{9.6294 \times 10^{30} - \nu^2}$$

The constants were calculated by the method of least squares so as to obtain the best possible values.

TABLE I

Wave-length	$(n-1)\times 10^8$ Observed	$(n-1)\times 10^8$ Calculated	Difference Calc.—Obs.
6707.85	77563	77556	−7
6438.47	77703	77697	−6
5790.66	78121	78123	+2
5769.60	78135	78139	+4
5460.74	78400	78402	+2
5209.08	78651	78655	+4
5085.83	78791	78791	+1
4799.91	79166	79156	−10

It will be seen from the last column that the agreement is very far from satisfactory, since the calculated dispersion curve is flatter than the observed curve. This divergence is commonly attributed to the omission of a second

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[1] Phil. Trans., 213, 1 (1914).

term in the formula, but up to the present no success, has been obtained with this dispersion formula with the addition of a second term.

The molecular phase hypothesis[1], however, leads to a simple modification of the Sellmeyer formula which expresses the refractivity of substances with remarkable accuracy and in the present paper its applicability to some gases may be dealt with. According to this hypothesis a pure substance at a given temperature and pressure is an equilibrium mixture of two or more phases of one molecule, each of these phases being characterised by a frequency which is an integral multiple of the fundamental frequency of the molecule. This fundamental frequency is situated in the infra-red region of the spectrum, whilst the phase frequencies lie in the visible or ultra-violet region. Since two or more phases are present the observed refractivity will be the sum of the effects due to these phases, the effect of each phase being proportional to its concentration. The following formula therefore is arrived at:—

$$(n-1)(V_1+V_2+V_3+\ldots.) = \frac{V_1N_1}{\nu_1^2-\nu^2} + \frac{V_2N_2}{\nu_2^2-\nu^2} + \frac{V_3N_3}{\nu_3^2-\nu^2} + \ldots \quad .$$

where V_1, V_2, V_3, etc. are the relative volumes of the phases present in the gas, ν_1, ν_2, ν_3, etc. their characteristic frequencies, and N_1, N_2, N_3, etc. are constants characteristic of the phases. Since the phase frequencies are integral multiples of the fundamental frequency characteristic of the molecule, the formula may be written in the form:—

$$(n-1)(V_1+V_2+V_3+\ldots.) = \frac{V_1N_1}{(a\nu_x)^2-\nu^2} + \frac{V_2N_2}{(b\nu_x)^2-\nu^2} + \frac{V_3N_3}{(c\nu_x)^2-\nu^2}$$

where ν_x is the fundamental frequency, and a, b, c, etc. are positive integers.

If the whole of the molecules present in the gas exist in one phase the formula is simplified to:— $n-1 = \dfrac{N_x}{(x\nu_x)^2-\nu^2}$.

so that the Sellmeyer formula in its simple form is applicable to this condition and this condition only. This formula for light of infinite wave-length becomes $(n-1_\alpha) = \dfrac{N_x}{(x\nu^x)^2}$

and we therefore have $N_x = (x\nu_x)^2(n-1)_\alpha$.

Since the value of $n-1$ for waves of infinite wave-length must be independent of the phases in which the molecules exist, the values of N_1, N_2, N_3, etc. must be equal to $(a\nu_x)^2(n-1)_\alpha$, $(b\nu_x)^2(n-1)_\alpha$, $(c\nu_x)^2(n-1)_\alpha$, respectively, and hence the complete dispersion formula becomes:—

$$(n-1)(V_1+V_2+V_3+\ldots.) = \frac{(a\nu_x)^2}{(a\nu_x)^2-\nu^2}V_1(n-1)_\alpha + \frac{(b\nu_x)^2}{(b\nu_x)^2-\nu^2}V_2(n-1)_\alpha + \frac{(c\nu_x)^2}{(c\nu_x)^2-\nu^2}V_3(n-1)_\alpha + \ldots$$

In this form the physical significance of the formula is rendered more apparent.

Now chlorine is known to exhibit only one absorption band in the ultra-violet at greater wave-lengths than 2100 A., which is the limit of a quartz spectrograph working in air. It must be remembered that this absorption

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[1] Baly: Phil. Mag., 40, 1; 15, (1920).

band has no apparent connection with the fine line absorption in the visible region, which moreover seems to have no influence on the refractivity since the dispersion curve is perfectly smooth and regular over the region wherein the fine absorption lines can be observed.

Since chlorine only shows one absorption band in the near ultra-violet it is probable that two terms in the above formula will be sufficient, that is to say there are only two phases present, one having its frequency in the extreme ultra-violet and not yet observed. For purposes of calculation the formula can therefore be simplified to

$$(n-1)(1+V)=\frac{N_1}{(a\nu_x)^2-\nu^2}+\frac{VN_2}{(b\nu_x)^2-\nu^2}.$$

where V is the relative volume of the molecules in the phase with larger frequency, the volume of the molecules with frequencies in the near ultra-violet being considered equal to unity. Now the centre of the first absorption band of chlorine lies at the wave-length 3380 Angstroms[1] or the frequency 8.876×10^{14}, but it must be remembered that the accuracy of this measurement cannot be guaranteed to within one Angstrom. Assuming in the first instance that the frequency of this absorption band is correct we have

$$(n-1)(1+V)=\frac{N_1}{(8.876\times 10^{14})^2-\nu^2}+\frac{VN_2}{(b\nu_x)^2-\nu^2}.$$

Where V, N_1, N_2, and $b\nu_x$ are unknown.

With a single dispersion curve we have not found it possible directly to determine these unknown quantities but have employed the following method of solution. As may readily be seen, the value of $b\nu_x$ may be determined if it be assumed that $N_1=N_2$, since if the dispersion curve is expressed by the formula it will equally well be expressed by

$$(n-1)(1+V^1)=\frac{N}{(8-8)6\times 10^{14})^2-\nu^2}+\frac{V^1N}{(b\nu_x)^2-\nu^2}$$

where V^1 is a constant. From the refractivities of chlorine for four different frequencies it was found that all the observed refractivities are expressed with considerable accuracy by the formula

$$(n-1)(4621.8)=\frac{7.948\times 10^{27}}{7.877876\times 10^{29}-\nu^2}+\frac{4620.8\times 7.948\times 10^{27}}{104.834\times 10^{29}-\nu^2}$$

The values of the phase frequencies ν_1 and ν_2 are therefore very near to 8.876×10^{14} and 3.23781×10^{15} respectively, and these must therefore be integral multiples of the fundamental frequency of chlorine. Now the ratio of these two frequencies is 3.6479 and the two smallest integers which have a ratio approximating to this are 197 and 54, the ratio of these integers being 3.64815. Assuming this ratio to be exact it is easy to calculate the constants anew in the formula

$$(n-1)(1+V^1)=\frac{N}{(54\nu_x)^2-\nu^2}+\frac{V^1N}{(197\nu_x)^2-\nu^2}$$

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[1] G. Ribaud: Ann. Phys., 12, 107. (1919).

where ν_x is the fundamental frequency of chlorine. The final values obtained were as follows:—

$$(n-1)(4650.6)=\frac{7\cdot945035\times10^{27}}{7\cdot873996\times10^{29}-\nu^2}+\frac{4649.6\times7.945035\times10^{27}}{104.79487\times10^{29}-\nu^2}$$

and the refractivities calculated from this formula are given in Table II.

TABLE II

λ	n obs.	n calc.	Difference calc.–obs.
6707.87	1.00077563	1.000775645	+0.000000015
6438.47	1.00077703	1.000777020	−0.000000010
5790.66	1.00078121	1.000781204	−0.000000006
5769.60	1.00078135	1.000781365	+0.000000015
5460.74	1.00078400	1.000783984	−0.000000016
5209.08	1.00078651	1.000786511	+0.000000001
5085.83	1.00078791	1.000787906	−0.000000004
4799.91	1.00079166	1.000791643	−0.000000017

The value of $(n-1)_\alpha$ given by the above formula is 1.000760158, and since $N_1=(n-1)_\alpha\times7.873996\times10^{29}=5.98548\times10^{26}$ and $N_2=(n-1)_\alpha\times104.79487\times10^{29}=7.96606\times10^{27}$, the value of V is at once found to be 349.6. The final dispersion formula for chlorine is therefore

$$(n-1)(350.6)=\frac{5\cdot98548\times10^{26}}{7\cdot873996\times10^{29}-\nu^2}+\frac{349.6\times7.96606\times10^{27}}{104.79487\times10^{29}-\nu^2}$$

The agreement between the calculated and observed values of the refractive indices is remarkably good and decidedly better than that obtained by the use of the approximate formula first used. There is no comparison between the results obtained by the new formula and those given by the simple Sellmeyer formula and set forth in Table I.

It may be noted that the first formula for chlorine was calculated on the assumption that the measurement of the central wave-length of the first absorption band was exactly 3380 Angstroms, but this is not necessarily correct to within one Angstrom. In the second and final formula the integral relation between the frequencies of the two absorption bands was taken as exact and the wave-length of the band was found to be 3380.8 Angstroms, the difference of 0.8 Angstrom being well within the limits of experimental error of measurement of this band. The agreement between the calculated and observed frequencies given by the formula establishes some confidence in its correctness, especially in view of the fact that the formula involves no new assumption beyond that the simple law of mixtures holds good with different molecular phases of the same molecule.

Before discussing the deductions to be made from the dispersion formula of chlorine the validity of the new formula may be tested on other gases, but unfortunately the accuracy of the refractivity measurements of other gases with absorption bands in the near ultra-violet is not as great as in the case of chlorine. The validity of the formula is however supported by gaseous bromine and by ozone.

In the case of bromine the refractivities observed and those calculated from a simple Sellmeyer formula are given in Table III.[1]

Table III

λ	$(n-1)\times 10^7$ obs.	$(n-1)\times 10^7$ calc.	Difference
6707.87	11525	11518	−7
6438.47	11570	11571	+1
6000	11662	11675	+13
5800	11735	11731	−4
5750	11741	11746	+5
5700	11762	11762	0
5600	11796	11767	−29
5460.74	11849	11842	−7

The absorption band of bromine vapour has its centre at $\lambda = 4210$ A[2] and hence the value of ν_1^2 is 5.077833×10^{29}. Using the same method as in the case of chlorine the following formula is obtained:—

$$(n-1)(79.798) = \frac{5.59538\times 10^{26}}{5.077833\times 10^{29}-\nu^2} + \frac{78.798\times 6.05302\times 10^{27}}{54.9314\times 10^{29}-\nu^2}$$

and the calculated refractivities are given in Table IV.

Table IV

λ	$(n-1)\times 10^7$ obs.	$(n-1)\times 10^7$ calc.	Difference
6707.87	11525	11520	−5
6438.47	11570	11570	0
6000	11662	11672	+10
5800	11735	11730	−5
5750	11741	11746	+5
5700	11762	11763	+1
5600	11796	11799	+3
5460.74	11849	11854	+5

The agreement is very distinctly better than in the case of the simple Sellmeyer formula.

In the case of ozone the refractivities given by Mr. and Mrs. Cuthbertson are obviously somewhat untrustworthy as these authors themselves point out, since the observations do not lie on a smooth curve. Before any use can be

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[1] C. and M. Cuthbertson: loc. cit.

[2] Ribaud: loc. cit.

made of these it is necessary to obtain the best approximation of the true dispersion curve of ozone and after plotting the observed values on squared paper the best possible curve was drawn through them. Now ozone exhibits an absorption band with centre at $\lambda = 2550$ A[1] whence $\nu^2 = 1.3840831 \times 10^{30}$. The dispersion curve is exactly expressed by the formula

$$(n-1)(4.9006) = \frac{6.7573 \times 10^{26}}{1.3840831 \times 10^{30} - \nu^2} + \frac{3.9006 \times 1.47159 \times 10^{28}}{3.0142257 \times 10^{31} - \nu^2}$$

The values of ν_1 and ν_2 are 1.176471×10^{15} and 5.49016×10^{15} respectively, and the ratio of these two numbers is 4.667 which is 14/3. The formula therefore can be written

$$(n-1)(4.9006) = \frac{6.7573 \times 10^{26}}{(3 \times 3.92157 \times 10^{14})^2 - \nu^2} + \frac{3.9006 \times 1.47159 \times 10^{28}}{(14 \times 3.92157 \times 10^{14})^2 - \nu^2}$$

The values given by this formula, which lie exactly on the dispersion curve are given in Table V together with the Cuthbertson observed values.

TABLE V

λ	$(n-1) \times 10^8$ calc.	$(n-1) \times 10^8$ obs.	
6707.87	50764	50764	0
6438.47	50957	50967	−10
5790.66	51567	51514	+53
5769.60	51592	51624	−32
5460.74	51993	52000	−7
5209.08	52394	52375	+19
5085.83	52657	52621	+36
4799.91	53249	53290	−41

Let it be assumed that the fundamental molecular frequency of oxygen is the same as that of ozone, and therefore the refractivity of oxygen should be represented by a formula analogous to that for ozone. On this assumption the ultra-violet absorption frequencies of oxygen will be integral multiples of the same fundamental frequency as that of ozone, namely 3.92157×10^{14}. It is well known that oxygen possesses an absorption band with centre near to 1900 A. and that these rays photochemically convert it into ozone. Now $4 \times 3.92157 \times 10^{14} = 1.568628 \times 10^{15}$ corresponds to the wave-length 1912.5 A. and this therefore may be taken as the centre of the band. The refractivity of oxygen can exactly be expressed by the formula

$$(n-1)(10.4157) = \frac{6.53793 \times 10^{26}}{(4 \times 3.92157 \times 10^{14})^2 - \nu^2} + \frac{9.4157 \times 8.00896 \times 10^{27}}{(14 \times 3.92157 \times 10^{14})^2 - \nu^2}$$

as can be seen from Table VI.

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[1] Ribaud: loc. cit.

The more refrangible band of oxygen therefore is the same as in the case of ozone and the frequency of the less refrangible band is four times the fundamental freuqency instead of three times as in the case of ozone. The different values of N_2 are due to the fact that $(n-1)_\alpha$ is different for the two gases. Although perhaps too much may not be claimed from this result in view of the inaccuracy of the observed refractivities of ozone, yet it may be said that the general validity of the new dispersion formula seems to be established.

TABLE VI

λ	$(n-1)\times 10^8$ calc.	$(n-1)\times 10^8$ obs.[1]
6562.82	26974.9	26975
5790.66	27098.8	27099
5460.74	27170.2	27170
4861.39	27345.1	27345

As regards the constants N_1, N_2, etc. in the numerators of the formula it has already been shown that these constants are the products of the refractivity for infinite wave-length into the square of the frequency of the absorption band. It follows from this, since the refractivity of a gas is directly proportional to the pressure, that $(n-1)_\alpha$ must be proportional to the density, the frequency of the absorption band being constant and independent of the pressure. Again, $(n-1)_\alpha$ must obviously depend on the nature of the gas and thus we may write for any gas

$$(n-1)_\alpha = D \times C,$$

where D is the total mass of the molecules in one linear centimetre and C is a fundamental constant characteristic of the gas. The value of $(n-1)_\alpha$ for oxygen is 0.000265705 and taking the number of molecules in 1 cc of oxygen to be 2.75×10^{19} and the mass of one molecule to be $1.56 \times 10^{-24} \times 32$, the value of C is found to be 1.7593×10^{12}.

The frequencies of the two absorption bands of oxygen, ν_1 and ν_2 were found to be $4 \times 3.92157 \times 10^{14}$ and $14 \times 3.92157 \times 10^{14}$ respectively, but it must be remembered that the fundamental frequency may be a sub-multiple of 3.92157×10^{14}. It is quite evident that this indeed is the case since no very strong absorption band is exhibited at that frequency. It is true that this frequency lies in the region covered by the A band of the solar spectrum, the corresponding wave-length being 7650 A, but the A bands are only observed with very great thicknesses of oxygen, that is to say the absorptive power is very small.

In the infra-red region between 15μ and 1μ oxygen only shows two very weak absorption bands at about 4.7μ and 3.2μ, and therefore the fundamental frequency must lie on the long wave-length side of 15μ. The frequencies of these two absorption bands must themselves therefore be integral multiples of the true infra-red frequency. Now the frequency $3.92157 \times 10^{14}/6 = 6.5359 \times 10^{13}$ corresponds to the wave-length 4.59μ and since the ac-

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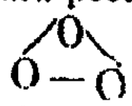
[1] C. Cuthbertson: Proc. Roy. Soc., 83, 151 (1909).

curacy of Coblentz's measurements cannot be guaranteed within 0.5% there is little doubt that this is the correct value of the wave-length of the absorption band he found at 4.7μ. In order to find the fundamental frequency of which the infra-red frequencies are integral multiples we may take the ratio of these two frequencies corresponding to 4.59μ and 3.2μ which is 1.43439. The two smallest integers which have a ratio near to this are 53 and 37, the ratio of which is 1.432, and assuming this to be correct the wave-lengths of the two bands are found to be 4.59μ and 3.204μ respectively, which are well within the limits of experimental error.

The infra-red fundamental frequency is at once found to be 1.7665×10^{12} a number which is strikingly close to the value 1.7593×10^{12} which was calculated above from the refractivity for infinite wave-length.

The value of $(n-1)_\alpha$ for ozone is found from the dispersion formula to be 0.000488214 and assuming the Avogadro constant to be the same as for oxygen the value of the characteristic constant C is found to be 2.10065×10^{12} which is materially greater than that of oxygen. Although too much stress cannot be laid on the relation between these numbers since the ozone value depends on the accuracy of the absolute determination of the refractivity for one wave-length, it would seem probable that in the ozone molecule an additional valency is called into play. This would perhaps lend more support to the formula $O=O=O$ than to the formual . The value of $(n-1)_\alpha$ for oxygen is far more trustworthy since the simple Sellmeyer formula which, according to Cuthbertson, expresses the refractivities of oxygen fairly accurately gives $(n-1)_\alpha = 0.000265308$ and $C = 1.7567 \times 10^{12}$ instead of 0.000265705 and 1.7593×10^{12} respectively.

The evidence afforded by the examples given above establishes some confidence in the correctness of the dispersion formula now brought forward. It may be noted that this formula, if proved to be correct, affords information which is of some importance. In the first place it defines the physical conditions existing in a gas, namely the number and the nature of the phases present and the relative volumes of each. In the second place it gives more accurate values of the characteristic absorption bands than can be arrived at by direct measurement. In the third place it leads to an accurate determination of the energy quantum characteristic of a molecule, this quantum being given by the product of the fundamental frequency of the molecule into the Planck constant.

Thus the formula given for chlorine states that this gas at 0° and 760 mm exists as a mixture of two phases of the chlorine molecule, the relative numbers of molecules in each being 10 and 3496. Each of these phases is characterised by an ultra-violet absorption band, the central wave-lengths of these being 3380.8 A and 926.73 A., respectively. The fundamental molecular frequency of chlorine is 1.64325×10^{13} which corresponds to the wave-length 18.2565μ and a strong absorption band should be exhibited at that wave-length. It is now known that chlorine does not exhibit any absorption bands in the infra-red at smaller wave-lengths than 15μ, but the longer wave region has not yet been examined. The molecular quantum of chlorine will be $1.64325 \times 10^{13} \times 6.56 \times 10^{-27} = 1.078 \times 10^{-13}$ erg per molecule, which is 1613 calories per gram molecule. The critical increment of chlorine in any of its reactions should therefore be 1613 calories or some multiple of this.

In view of these deductions from the dispersion formula of chlorine it may be noted that these depend within limits on the relative values of the refractivities for different wave-lengths and not on the absolute values. The correctness of the value of $(n-1)_\infty$ and hence of the constants N_1 and N_2 in the formula depend on the latter. Since Mr. and Mrs. Cuthbertson do not claim a greater accuracy than 1 in 1000 for the absolute refractivity of chlorine which they determined for $\lambda = 5460.74$, we have not discussed the value of $(n-1)_\infty$ for this gas. The relative values are, however, far more accurate and justify the deductions drawn above.

The University of Liverpool.

NEW BOOKS

Synthetic Resins and their Plastics. *By Carleton Ellis. 23×16 cm; pp. 514. New York: The Chemical Catalog Company, 1923. Price: $6.00.* In the preface the author says: "Vast quantities of resins are needed to meet the world's requirements and the winning of resins from natural sources for various reasons is uncertain. The supply of fossil resins is by no means abundant and reports from some quarters sound an ominous note of approaching exhaustion of the sources of these resins. One need but turn to old formula books to find receipts for making varnishes from amber and other resins now so rare as to be sold only by the ounce. The significance of this observation is that it denotes the passing, from time to time, of raw materials once relatively abundant. Moreover, it marks the entry of synthetic resins into the market and heralds the activity of research chemists who already have demonstrated that it is possible not merely to equal but in many cases to outdo nature by producing synthetically resins having properties greatly desired but not heretofore found in natural products."

The chapters are entitled: introduction; need for synthetic resins and types desired; cumaron and indene resins; commercial grades of cumaron resin; their uses and identification; modern methods of producing cumaron resin; resins from petroleum—polymerization of certain unsaturated hydrocarbons; the resinous condensation products of phenols and aldehydes; phenol-formaldehyde resins—bakelite, condensite, redmanol, and miscellaneous phenol-formaldehyde resins; phenol-formaldehyde resins—use of modifying agents; applications of phenol-formaldehyde resins; aldehyde resins; furfural resins; ketone resins—acetone resins; urea and thiourea resins; resins from wood and wood distillation; hardened rosin and resinates; ester gums or artificial resin esters—spar varnishes; resins from polybasic acids and polyhydric alcohols—glycerol polybasic acid resins; polymerization of vinyl compounds—effect of substitution in the ethylene group; sulphur resins; nitro resins; halogenated rubber—chlorinated rubber solutions; miscellaneous resins; certain resinous products derived from fatty oils; preparation and properties of plastic molding compositions; equipment for molding plastic compositions; methods of molding; test and quality of molded articles.

"A synthetic resin is a complex, amorphous, organic, semi-solid or solid, material, usually a mixture of substances; built up by chemical reaction, and approximating the natural resins in various physical properties; namely, lustre, fracture, comparative brittleness at ordinary temperatures, insolubility in water and fusibility or plasticity when heated and exposed to heat and pressure but commonly deviating widely from natural resins in chemical constitution and behavior with reagents," p. 13.

"Among the artificial resins, cumaron resin may be considered of prime importance. Since the resin is produced simply by polymerization rather than by reaction between two or more chemically dissimilar substances it falls into the class of strictly *polymerized products* and not into the synthetic domain represented, for example, by such resins as those from phenol and formaldehyde. Upon decomposing the resinous polymer by means of heat or destructive distillation cumaron resin yields the constituents from which it has been derived while the decomposition by heating of many other resins yields products differing greatly from the raw materials used in their making.

"Cumaron resin is used for varied purposes and while in a certain measure restricted by its nature, progress is being made toward extending its applicability. One reason for its relatively limited use at the present time is that the manufacturers of the resin have changed their method of manufacture in endeavoring to obtain a better product; conforming with the changed practice in the production of the raw material. During the late war the coke ovens were run under forced and abnormal conditions and cumaron resin, which was prepared from the naphtha obtained at that time largely from this source, differed to some extent from that produced later when the ovens were run under normal conditions. Curiously, the resin obtained during the War produced a satisfactory product when used in rubber, chewing gum, varnishes, etc. but that produced directly after the War behaved erratically. In rubber, chewing gum, and varnishes detrimental effects such as exudations, "bloom", etc., were noticed. This condition naturally discouraged the consumers of cumaron resin considerably. The difficulty, however, was subsequently remedied by the manufacturers of the resin and the present-day resin is eminently satisfactory for these purposes but there has been difficulty in assuring the consumers of this fact. However, the use of the resin in the production of a varied number of products is gradually increasing as consumers are educating themselves to its utility and already cumaron resin successfully competes with resin ester in the preparation of varnishes. In the compounding of rubber, printing inks, etc., the resin exhibits important properties which render its use advantageous. At the present time the production of cumaron is in excess of the demand and this has been true throughout its history in the United States. In Germany, because of the embargo during the War, cumaron was used to replace the natural resins to a great extent, and there the demand was greater than the production but since this period its use and production have diminished considerably," p. 39.

"During the latter part of the decade, Baekeland began an investigation of the resinous condensation products of phenol and formaldehyde, which brought forth yet another modification of these resins. He improved the methods of hardening under heat and pressure so that rigid-molded articles could be very readily obtained. The result of his investigations was the commercial development of the molding composition and product known as Bakelite. A great variety of application have been made of phenol-formaldehyde resins or resinoids ranging from the manufacture of a billiard ball to wireless telegraphic apparatus; from the manufacture of a self starter for automobiles to transparent fountain pens and artificial amber. The range of applications also embraces such articles as switchboards for battleships, molded parts for kodaks, phonograph records, casings for instruments of precision, armatures and commutators for dynamos and motors, telephone receivers, railroad signalling devices, grinding wheels, umbrella handles, buttons, cigar holders and pipe stems and ornamental articles.

"To a notable extent the uses to which phenol-formaldehyde resins have been put in the plastic field have been spectacular ones and these products of late years during the period of commercial development and expansion have therefore been particularly before the public eye. Such varied applications as radio apparatus, billard balls, pipe stems, beads, fountain pens and other articles constantly in evidence have led many to believe the importance of these resins in the plastic field is greater than the actual consumption of such products would warrant. Aside from the two most important organic plastics,—namely rubber and celluloid,—other plastic compositions, particularly those made from shellac and the pitch or asphaltic compositions made by the cold-molding process, are employed in greater quantities than those having as a basis phenol-formaldehyde resins. Owing to the enormous demand for shellac in the production of phonograph records this binder ranks at the head of the list in point of consumption of resinous plastics. Next in importance from this standpoint is the cold-molded material. In both these fields the consumption is greater than in the case of the phenol-formaldehyde resins," p. 92.

"The reaction between phenol and formaldehyde, in so far as condensation is involved, is initiated or accelerated by acid and basic substances. As may be expected strong mineral acids and caustic alkalies in general are the most vigorous catalysts, but for many purposes such substances are not compatible with the uses to which the final product is to be put. Both strongly basic and acidic catalysts when used in large proportions affect metals, cause deterioration of filler and attract moisture, thus lowering the dielectric properties of the composition. Weaker mineral acids, organic acids, acid and basic salts also have been recommended. Ammonia and ammonium compounds, ammonium derivatives, hydrazine and various amines, such as aniline and benzylamine likewise have been proposed and some of these find application in commercial operations. Ammonia and certain of the amines are most favored as no objectionable degree of acidity or alkalinity remains in the final product. When ammonia is employed, as may be expected, it reacts with formaldehyde to yield hexamethylenetetramine and as this in turn reacts with phenol, ammonia is set free. Although ammonia is less objectionable than fixed alkalies as a permanent constituent of artificial amber and molded articles some means of neutralizing and fixing it would be desirable. Molded articles containing a considerable amount of ammonia are likely to blister when heated to temperatures at which the resin binder itself would otherwise be unimpaired. Aylsworth has proposed the addition of phthalic anhydride or other organic acid anhydrides as means of neutralizing free ammonia," p. 132.

"Livering is a peculiar thickening which occurs when basic pigments, and, more especially, zinc oxide, are ground with certain varnishes. In its more characteristic stage this thickening assumes a liverlike consistency. It is due to various stages of gelatin of the vehicle, and may occur immediately after grinding with the pigments or after storage for a longer or shorter time. The first is due to a purely physical reaction, occurring when a varnish containing a highly polymerized oil or gum, which is peptized (held in "solution") by resin acids, is mixed with basic pigments. This is due to the fact that a very large proportion of the free acid is absorbed by the pigment surface, and, since nothing is then left to prevent the colloids from gelling, the inevitable happens.

"The phenomenon is usually only troublesome when zinc or titanium oxides are present. With the other basic pigments gelation is usually deferred for weeks until the resin acid has reacted chemically with the oxides or carbonates. Gelation then occurs. There are other causes of thickening on storage which do not concern us here.

"It will be seen, then, that free resin acid is something to be avoided in paint and varnish products. Rosin which has been treated with lime is, however, not entirely reliable as cases are on record of livering occurring in paint or enamel made from hardened rosin after standing for several months," p. 258.

"Ester gums to a large extent have displaced the copal gums in the manufacture of spar varnishes. A rosin ester Chinese wood oil varnish is notably waterproof and even will resist the action of hot water for a considerable period. The discovery of the valuable properties of the combination of ester gums and Chinese wood oil has created a noteworthy change in varnish making. In fact, specifications for spar varnishes have been modified in numerous instances in order to secure an ester gum varnish in preference to one made with hard fossil resins," p. 271.

"Hardened steel is perhaps the most universally used material for molds employed in plastic molding. Since the cost of designing, fabricating and maintaining molds is very high it is worth while in most cases to use hardened steel. Although the initial cost may be considerably higher than that of steel not hardened, the longer life of this type of mold and the lower cost of maintenance more than make up the difference in cost of fabrication. Hardened steel is economical especially when large quantities of articles are to be molded and when the design has been proved to be thoroughly efficient. In cases when a relatively small production is required or when the design of a mold is of doubtful efficiency steel, *not hardened*, is employed because in the making of the mold slight changes may be made easily in many cases. The *unhardened* steel mold, however, will require polishing oftener and if used in constant production will have to be discarded comparatively soon due to the wear and tear in general handling. In some cases gray iron castings have been used for molds where the peculiar or irregular shapes desired make steel difficult to shape. Gray iron castings are of course very brittle, cannot be well polished and their life is comparatively short. Molds for special purposes have been made of bronze and aluminum alloys and in the last few years in the molding of printing plates a "molded mold" made from synthetic resin with a thin metallic foil on the molding surfaces has been employed with satisfactory results. This type of mold has a very limited use," p. 398.

Wilder D. Bancroft

Fundamentals of Organic and Biological Chemistry. *By T. G. Phillips. 20×14 cm; pp. xi+260. New York: D. Appleton and Company, 1923. Price: $2.00.* In the foreword Dean Vivian says that "it is now evidently impossible for any one person to master all the information in all of the sciences, and even within each science the advanced student finds it necessary to devote his major effort to a more or less restricted area of the general field of that science. The different sciences are so closely interlocked, however, that the student of one science finds it necessary to have some knowledge of all the others. . . . The short course in science has been in bad repute in the past largely because the method of shortening the course consisted in an attempt to cover the entire field of the science in a superficial way. . . The better way to construct a brief course is to avoid trying to cover the entire field of the science and to select for presentation those fundamental facts and principles which will function in the life work of the student for whom the briefer course is arranged."

The chapters are entitled: the hydrocarbons; the alcohols and ethers; the aldehydes and ketones; the acids and acid chlorides; esters and fats; mixed compounds; the carbohydrates; unsaturated and aromatic compounds; nitrogen compounds; the proteins; the general chemistry of living organisms; the chemistry of plants; the chemistry of animals.

The author is quite clear as to the importance of photosynthesis, p. 209. "Thus by this process of photosynthesis, green plants are able to manufacture their own organic food with the aid of the energy furnished by the sun. But the importance of the process is much greater than this would indicate. All other plants, and all animals, either directly or indirectly, use green plants as their only source of food. Thus green plants supply the organic building material and energy for all living organisms. Not only does photosynthesis furnish the energy which makes life possible, but also wood, coal, petroleum, and gas are products of green plants. With the exception of water power and wind, all energy used in heating and lighting, in running automobiles, railroads, and factories, was derived from the sun and stored in the form of reduced carbon compounds by the process of photo-synthesis carried on by green plants in bygone ages."

The page on bacteria and fungi is also interesting, p. 218. "The most important of the plants of this kind are those that are very small and relatively simple in structure, belonging to the two great groups, bacteria and fungi. The bacteria are single-celled organisms, the fungi include both single-celled species and those of more complex structure. Most of them are small, but some forms, such as toadstools and mushrooms, attain a considerable size.

"These plants themselves or the spores that many of them form are present practically everywhere. Whenever conditions such as food supply, moisture, and temperature are favorable for them, they grow rapidly, bringing about very decided changes in the medium in which they grow. They digest the organic foods that are available, and use part of the products of digestion for respiration and part for growth. Since they are not able to rebuild organic food with the storage of energy from the sun, the net result of their activity is destructive.

"They are the most important agencies in the decay of plant and animal remains. Decay is a process of oxidation caused by the respiration of these organisms, resulting in the formation of carbon dioxide and water from the organic substances they use as food. The continued accumulation of plant and animal remains would soon result in the exhaustion of the carbon dioxide of the air, and the growth of green plants would cease. But, due in large part to the activity of bacteria and fungi, these organic remains are oxidized, their potential energy is liberated, and the carbon they contain is returned to the air as carbon dioxide, making possible again the growth of green plants, the formation of a new supply of organic compounds, and renewed storage of energy from the sun."

The author is not certain that the minimum protein requirement is necessarily the best, p. 242. "With proper care in the selection of foods, it is undoubtedly true that a very great reduction in the protein intake may be made safely; in many cases the health has been improved remarkably by this means. There is no doubt that many Americans eat very much more protein than Voit's estimate of 120 grams a day, and often to the detriment of their health. There are, however, some facts that make doubtful the value of decreasing the protein intake very greatly. It is well known that the most progressive races consume relatively large amounts of protein, but it is uncertain whether this is necessarily true."

The question of net energy is one that is not always considered, p. 250. "Not all the metabolizable energy may be of use to the body for maintenance, growth, or production. This is due to the fact that the ingestion of food results in increased heat production. The exact reasons for the increase are not known. Part of it is due to the work of mastication, a little to the movement of the walls of the stomach and intestines during digestion, and perhaps a small part to the work of secretion of digestive fluids by the glands. The greater part of this energy cannot be accounted for in these ways, but seems to be due to a stimulating effect of the food itself on oxidation, resulting in the production of excess heat, which is lost by radiation or evaporation and appears to serve no essential function in the body. Whatever the cause, a very considerable portion of the available energy of the food is lost in this way, and its amount varies widely for different foods. The energy remaining after subtracting this from the available energy is called the net energy of the food, and is the real measure of the value of a food as a source of energy."

Wilder D. Bancroft

Everyday Mysteries. *By C. G. Abbott. 20×14 cm; pp. xi+198. New York: The Macmillan Company, 1923. Price: $2.25.* In the introduction Slosson says that "it is the aim of the Young People's Shelf of Science to present modern views of the several sciences in a comprehensive and attractive form. These books are intended to be read rather than to be studied. They are not designed to be tasks, but recreations. They do not follow the conventional classification of the college, but treat of natural and industrial processes from a novel and practical viewpoint. They show that science is not a remote and recondite study but a part of everyday life, the unseen foundation of all that we see and do."

The single sketches are entitled: what comes out of the spigot; the plumber's surprise; the little spoilers; something about soap; fixing the clock; doorbells and their relatives; the homemade forge and bicycle; down by the brook; blueberries; pots and pans; saving half the coal pile; rags and velvet gowns; bread and cheese; how deep is the ocean?; the divided crown; the story of the old shoes; the early morning visitor; cooking by sun rays; how the sun makes plants grow; the two-cent investment.

The book is a success and both the editor and author are to be congratulated. There are surprisingly few slips. The account of the boiling-point, p. 3, is a bit shaky and the paragraph on the electrical properties of water, p. 8, is certainly misleading. White of egg is not what is used with bichromate, p. 194, and the reviewer wonders whether the upper door of the furnace should really be kept closed hermetically, p. 102. It is undesirable to sweep the hot air up the chimney too rapidly; but if one only burns the coal to carbon monoxide, one is wasting about half the heat and the saving is imaginary.

Using aluminum sulphate as fertilizer for blueberries to produce an acid soil was new to the reviewer, p. 91, though he ought to have known about it, and even if one does not wish to grow blueberries it is a distinct achievement to grow rhododendrons and laurel really well.

Wilder D. Bancroft

A GENERAL FORMULATION OF MOVEMENT IN AN ELECTRICAL FIELD: MIGRATION, ELECTROPHORESIS AND ELECTROÖSMOSIS OF SODIUM OLEATE.

BY MARY EVELYN LAING

The object of the present investigation is to demonstrate the fundamental similarity between various processes of electrolytic conduction usually considered as separate phenomena. The attempt will be made to show that the phenomena of electrolytic conduction, electroösmosis and electrophoresis are but special cases of an inherently identical process. It appears possible to develop a general theoretical treatment embracing ions, membranes and all charged particles and surfaces alike. This involves an enlarged conception of the electrical double layer and the abandonment of some of the currently accepted formulae of Lamb and Helmholtz.

A unique material for the purpose of this investigation is afforded by sodium oleate solutions by the fact that portions of one of its solutions may be studied side by side in the three forms of sol, jelly and opaque curd as shown by Laing and McBain.[1] Extensive measurements will be presented to prove that the movement of the various constituents of the soap system relative to the solvent is the same for clear sol and colourless jelly and that it is likewise independent of whether the solvent moves through the jelly or particles of jelly or curd move through the solvent.

The main results of the study of soap solutions are supported by the quantitative agreement of many lines of evidence. It is however necessary to submit them to even more searching tests. Again it is desirable to obtain information as to the effects of the electric current in order to get further insight into the structure and theory of colloidal gels. Every method of investigation not only adds something further to our knowledge of soaps but it also renders more precise the interpretation of previous data.

One may take this opportunity of noting that the constitution deduced for soap solutions although expressed for convenience in terms of the Arrhenius Dissociation Theory is substantially the same when expressed in any of the hypotheses of the 100 per cent ionisation of strong electrolytes.

Theoretical

It was pointed out by McBain and Salmon[2] that the very fact of the existence of the ionic micelle must lead to a freer conception of the electrical double layer and ultimately to a general theoretical treatment embracing ions and all charged surfaces alike. The most striking property of the ionic micelle is the very high electrical conductivity of each of its many charges as well as the unimpaired conductivity of the corresponding sodium or potassium ions.

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[1] J. Chem. Soc., 117, 1506-1528 (1920).

[2] J. Am. Chem. Soc., 42, 426 (1920).

The electrokinetic phenomena of colloids and surfaces have been extensively studied for over a century, electroösmosis and electrophoresis being simultaneously discovered by Reuss in Moscow in 1808, and much of our knowledge is due to the quantitative studies of Wiedemann and of Quincke.

There are four ways in which charges on surfaces may be manifested, namely; movement of a suspension in an electric field, (electrophoresis in the nomenclature of Ralston) and movement of solution past the solid when the latter is fixed, as in the case of a diaphragm or capillary, (electroösmosis); likewise electromotive force which is set up when the liquid is forced past the solid (Quincke's diaphragm current) or similarly when a finely-divided charged solid falls through a liquid.

The voltages produced by the streaming of liquid past surfaces or of powders through liquid are related to the mobilities and charges in precisely the same way that such potentials as diffusion potential are related to ionic mobilities. It is clear that these relationships are the converse aspect of the generalisation here made that electroösmosis and electrophoresis (of which this paper chiefly deals) are but particular cases of electrolytic migration. One result of this work will be to emphasize that the distinction between these processes is largely artificial and that they are both governed by the same laws as the movement of ions.

The modern view explains the charges on the solid by assuming with Freundlich[1] and Bancroft[2] that ions have been adsorbed. Little or nothing is usually said about the corresponding ions of the outer layer which we hold to be of almost equal importance whether in discussing electrokinetics or colloids.

The Proposed New Formulation

In the experiments herein described I have endeavoured to present the various electrokinetic phenomena in a more tangible way, presenting them directly as a particular case of electrolytic migration and expressing them in terms of mobility without reference to the many hypothetical assumptions usually introduced into the evaluation of the electrical phenomena of colloids.

Movement of charged carriers is identical with electrolytic conduction. All carriers whether ions, particles or surfaces must therefore impart conductance to the system. The ionic micelle is only a particularly striking case of an "electrical double layer" where the conductivity of both parts of the double layer has been at last taken into account and it clearly indicates that the participating ions and surfaces retain an unimpaired electrical conductivity. This at once brings the whole problem of electrophoresis into the field of electrolytic migration.

Helmholtz' own description of the behaviour of the double layer is as follows:

"On the whole the algebraic sum of the two equals zero, and the centre of gravity of the complete system, solid particle and surrounding positively

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[1] Z. physik. Chem. 79, 385, 407 (1912).

[2] J. Phys. Chem. 16, 312 (1912).

charged fluid layer taken together, cannot be moved by the electric forces which arise from the potential fall in the liquid through which the current passes. However, the electric force will tend to bring about a displacement, relatively to each other, of the positively charged fluid layer and the negatively charged particle, whereby the fluid layer follows the flow of positive electricity while the particle moves in the opposite direction. If the liquid were a perfect insulator the new position would still be a condition of equilibrium. Since, however, through the displacement of the layers the equilibrium of the galvanic tension between the solid particle and the liquid is disturbed, and on account of the conductivity of the liquid always seeks to restore itself, the original state of electrical distribution will tend to be continually reproduced and so new displacements of the particle with respect to the surrounding liquid will continually occur."

We have a much clearer knowledge of what is meant by the conductivity of the liquid, which is, the free mobility of the charged particles or ions themselves, a conception which was impossible to Helmholtz before the advent of the dissociation theory. We see now that the conductivity is identical with the mobility of these free ions and we are therefore able to read into Helmholtz' old words a much freer conception of the double layer than has hitherto been held. (It is likewise interesting to observe how his Faraday lecture delivered in 1885 reads as though he had been an exponent of one of the recent 100 per cent ionisation theories.)

The essential feature in electroösmosis, electrophoresis and ionic migration is, in each case, the relative movement between solvent and carrier. For an electrolyte it is expressed by the Hittorf migration number

$$n = \frac{v}{u+v}$$

Actually there is a term involved in this expression which does not appear as it cancels out from numerator and denominator, namely concentration. This becomes clear if a mixture of two simple electrolytes such as potassium chloride and iodide is considered. Here the movement of the iodine relative to the water is expressed as follows

$$n_I = \frac{c_I v_I}{c_K u_K + c_{Cl} v_{Cl} + c_I v_I} = \frac{''cv''}{c'u' + 'cu' + ''cv''} = \frac{''cv''}{\mu}$$

where c_I or $''c$ is the concentration of the iodine ion.

c_{Cl} or $'c$ is the concentration of the chlorine ion.

c_K or c' is the concentration of the total potassium ion. μ is the conductivity in reciprocal ohms of that amount of solution containing 1000 gms solvent and c_I equivalents of iodine ion and is equal to the sum of each ion mobility multiplied by its concentration, i.e. the equivalent conductivity of each ion times its concentration in equivalents.

For purposes of electrolytic migration it is most convenient to express concentration in weight normality, i. e. equivalents per 1000 gms. water, since all accurate migration data are necessarily calculated with reference to pure solvent.

We now propose a universal formula for the transport of matter accompanying the conduction of electricity through any system, metallic conduction alone excepted.

$$n_1 = \frac{c_1 m_1 f_1}{c'u' + c''u'' + \ldots + {}'cv' + {}''cv'' + \ldots c_1 f_1 + c_2 f_2} = \frac{c_1 m_1 f_1}{\mu}$$

$$''n = \frac{''cu''}{\mu}$$

$$n' = \frac{c'v'}{\mu}$$

etc.

The bodily transfer or migration of any constituent of a solution is proportional to its concentration and its conductivity divided by the total conductivity of the solution. There will be one such expression for each conducting constituent whether crystalloidal or colloidal and whether positively or negatively charged.

For an ordinary anion whose concentration is $''c$ and mobility u'', the transport during the passage of one faraday (96500 coulombs) will be

$$''n = \frac{''cu''}{\mu}$$

For a colloidal particle or even a large diaphragm, the formula will be

$$n_1 = \frac{c_1 m_1 f_1}{\mu}$$

where c_1 = number of chemical equivalents per 1000 gms. of solvent.

m_1 = number of chemical equivalents which carry one electrical charge.

f_1 = conductivity in reciprocal ohms of one chemical equivalent.

μ = total conductivity as before = sum of concentration of each conducting constituent multiplied by its mobility.

In general where there are several cations, anions or colloidal constituents the migration of any constituent will be

$$n = \frac{c\,m\,f}{\mu} = \frac{\text{effective mobility of that constituent}}{\text{total conductivity of all constituents.}}$$

and the general formula may be written

$$n_2 = \frac{c_2 m_2 f_2}{c'u' + c''u'' + \ldots {}'cv' + {}''cv'' + \ldots c_1 f_1 + c_2 f_2} = \frac{c_2 m_2 f_2}{\mu}$$

μ = the conductivity in reciprocal ohms of the amount of system containing 1000 gms. of solvent.

It follows at once from this that conversely the movement of solvent past the constituent (electroösmosis) must be

$\frac{m_2 f_2}{\mu}$ kilos of solvent per faraday of current.

There would seem to be no restriction upon the application of these formulae except that the composition of the system must be taken at right angles to the path of the current so that the formula then includes even the walls of the vessels in which the solution is contained.

The general distinction between a true ion on the one hand and a colloidal particle, diaphragm or wall on the other, is that in the latter cases n is usually a very large number. In the ionic micelle of soap solutions it will be found that m only slightly exceeds unity, that is, one electrical charge for nearly every oleate radicle in the micelle. For nickel in benzene Hatschek obtains $n = 5000$, evidently owing to the high value of m and the small value of μ.

The product m_1f_1 may be termed the effective mobility since it is the conductivity in reciprocal ohms of that amount of colloid that carries one equivalent of electrical charge. If f_1 (the conductivity per chemical equivalent) is very small, m can be very large without the effective mobility being even as high as that of an ordinary ion. For instance in the case of the neutral micelle or undissociated soap the value of mf will be shown to be 18.3 reciprocal ohms whereas Bredig[1] found the lowest value for a true organic ion of high molecular weight was 20.7. In this sense then the effective movement under any particular conditions is almost that of a simple univalent organic ion of high molecular weight in spite of its equivalent conductivity being probably very minute.

It was pointed out by Müller[2] in 1907 that the electrophoretic mobility of a colloid expressed in cm. per volt per cm. per sec. is almost as great as that of a slow-moving organic ion, which is exactly what is found here for undissociated colloidal soap in spite of its negligible conductivity.

The number of equivalents m of neutral soap which carry one faraday is very large but unknown and equally unknown is the mechanical structure and resistance experienced by a simple colloidal particle.

It is evident from inspection of the formulae that they are not merely formal expressions embracing only current knowledge but that they include at least two new points accessible to experimental test. The first is that the conductivity of the free outer ions of the so-called double layer is clearly taken into account. The second is that electrophoresis and electroösmosis are inversely proportional to the actual conductivity of the solution.

There are many experiments in the literature purporting to describe the effect of additions of salts on the charge of colloid particles and diaphragms as measured by electrophoresis and electroösmosis which are obviously invalid if these equations are true, since the effects may be largely or entirely due to increased conductivity μ.

Again it may be noted that a possibility is suggested for the determination of both m and f and not merely of their product. This arises from the fact that m occurs only in the numerator and not in the denominator and it should

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[1] Z. physik. Chem. 1894, 13, 191 (1894).

[2] "Allgemeine Chemie der Kolloide".

therefore be possible to deduce the value of *m* in experiments in which the denominator is varied as for example by the addition of suitable electrolytes.

The relation between migration and electroösmosis may be stated as follows. The movement of a true ion and the electrophoresis of a colloidal particle is each proportional to the slope of potential and likewise to the time. If both are present in the same solution, owing to the incomparably greater conductivity possessed by a true ion or an ionic micelle over that of any ordinary colloidal particle, and since the amount of current passing is governed by the conductivity of the solution, the duration of the experiment, (that is, the time required for one faraday of current to pass) depends upon the ions. Thus if the ions in one solution conduct 10 times better than in another, the same colloidal particle being present in both and the same E. M. F. being employed, the duration of the first experiment for a definite amount of electrolysis will be one tenth that of the second and the colloidal particles will only have time to exhibit one tenth of the movement.

If the excess of free ions could be eliminated altogether the residual conductivity would be due only to colloidal particles and their corresponding ions and the experiment would be continued as long as was necessary to pass a faraday of current. The electrophoresis would now appear in terms of effective mobility.

Application to Soap Solutions

In a solution of sodium oleate (the hydroxyl ion being negligible), there is one cation, namely $Na^{\cdot}$, one anion Ol' and two negatively charged colloidal constituents, namely ionic micelle and neutral micelle.

The transport of ionic micelle is

$$n_1 = \frac{c_1 m_1 f_1}{c'v' + {}'cv' + c_1 f_1 + c_2 f_2}$$

$$= \frac{c_1 m_1 f_1}{c_{Na} u_{Na} + c_{Ol'} v_{Ol'} + c_{1.\text{micelle}} v_{1.\text{micelle}} + c_{\text{neutral micelle}} v_{\text{neutral micelle}}}$$

where m_1 = slightly greater than unity.

$m_1 f_1 = 64.3$, $u' = 43.6$ and $v' = 20.7$ and f_2 is negligible.

The total movement of all negatively charged constituents which all contain oleate radicle

$$n = \frac{{}'cv' + c_1 m_1 f_1 + c_2 m_2 f_2}{\mu}$$

This shows quite clearly how the observed migration number in soap solutions is made up of the movement of the separate constituents which move each at a different rate, the ionic micelle nearly four times as fast as the neutral colloid or the simple oleate ion. In the more concentrated solutions the simple oleate ions disappears.

Experimental

The only trustworthy method of determining mobilities in doubtful or difficult cases is the original analytical or Hittorf method, which gives the

Hittorf migration number. G. N. Lewis[1] and Lash Miller[2] have shown that the moving boundary method of Abegg, Denison and Steele does not give the true transference number as originally asserted but only the apparent Hittorf number and it is neither as accurate nor as conclusive.

Experimental difficulties are somewhat great in the case of sodium oleate solutions, since the transition from one state to another is affected by temperature, previous history of sample, duration of run, age, etc., and it was necessary to use elaborate care so that the measurements made might be trustworthy and moderately accurate.

The electrodes were protected by guard solutions of sodium sulphate in the anode and cathode compartments to prevent unknown and uncontrollable reactions at the electrodes. Frothing was thus avoided by keeping the soap from direct contact with the electrodes. Further the presence of sulphate in the cathode portion retarded the migration of OH' by lessening its relative concentration. The one essential condition of the Hittorf method is that the middle portion should be unchanged so that all changes are confined to the electrodes and are directly susceptible to analytical measurement. Sulphate was never found in the middle portion.

The old custom of analysing only one, two or at most three portions is unsatisfactory, for the basis of migration work consists in the maintaining of the middle portion unchanged so that ions leaving and entering it are the same. In the case of soap sols, it was found advisable to analyse seven portions in order to follow with more certainty the changes in concentration throughout the apparatus. In soap jellies and curds convection does not occur and hence sometimes only anode and cathode portions were studied but in other cases solid was cut out of the middle and analysed. Silver coulometers were used at each end of the apparatus to detect any leakage of current but they always agreed within 0.01%.

Analyses were made for both constituents (sodium and fatty radicle) of the soap solutions in all portions so that each experiment gave four semi-independent determinations of the migration number. In very few instances in the whole literature has a measurement been made of the movement of both anion and cation and in this case the fact that the two together are found to account for the total current affords a useful check on the possible nature of the ions in solution.[3] For instance, the effect of hydrolysis alkalinity is seen to be negligible in conformity with previous work.

The Apparatus employed for the Sol

The migration apparatus for all except the most dilute solutions consisted of three U-tubes (see Fig. 1) made from one centimetre boro-silicate tubing of uniform bore, (so that the current may pass without uneven heating effects), united by ground joints. The total capacity was 130 cubic centimetres. The

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[1] J. Am. Chem. Soc., 32, 864 (1910).

[2] Z. physik. Chem., 69, 437 (1909).

[3] McBain and Coleman: Trans. Faraday Soc., 15, 1-20 (1919).

platinum electrodes were sealed in to the hollow-ground stoppers. The tubes were cleaned before each experiment with bichromate solution mixture.

The apparatus has first to be set up with sodium sulphate solutions without contaminating the rest of the apparatus. By momentarily loosening the rubber stoppers the solution is allowed to go round the bend to the required extent (which is further in the case of the anode). This is necessary since the soap solution floats on top of the sulphate. When the outside legs have been filled nearly to the top the electrode stoppers are replaced, all vaseline removed from the stoppers and the tube weighed. The three U-tubes are now put together and mounted on a stand.

Soap solution is now placed in the apparatus but the first portion in the anode and cathode compartments have to be introduced through a capillary pipette with upturned flaring tip held just in the surface of the liquid so as to avoid any mixing of sulphate and soap solutions. The levels are equalised and stoppers vaselined and closed. Fifteen minutes is allowed in the thermostat before turning on the current. A glass-sided thermostat permitted in most cases observations of the distance travelled by the boundaries of the soap solutions. Convection is small owing to the viscosity of the solutions.

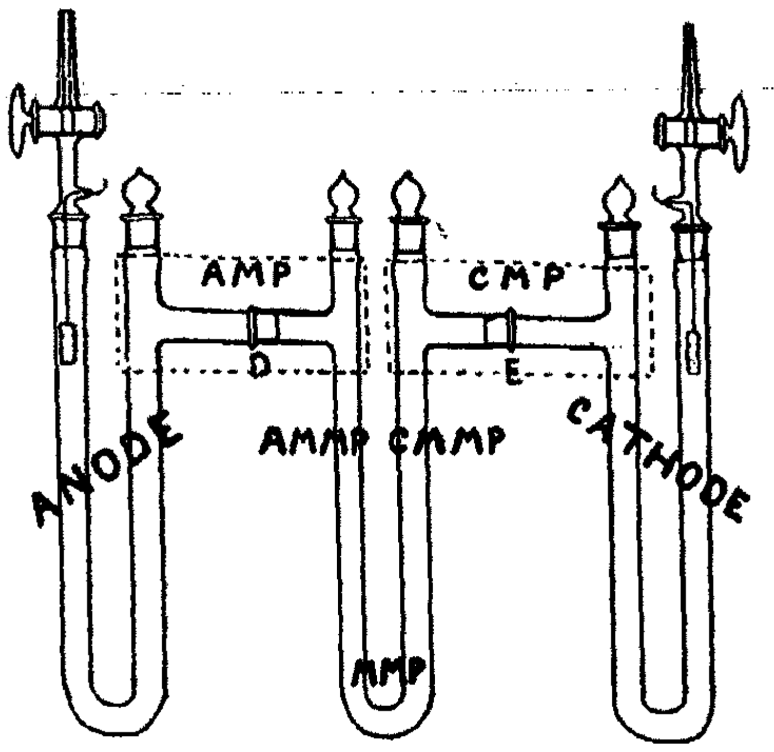

Fig. 1
Scale about 1:3

At the conclusion of the experiment five consecutive middle portions are removed by means of pipettes for weighing and analysis. Each pipette is first rinsed out with a sample of the solution from that portion. The boundaries of the portions are indicated by the dotted lines in the figure.

The anode and cathode tubes are then detached and weighed after the glass stoppers and joints have been freed from vaseline, and the ground ends have been closed with rubber stoppers. This gives the weight of the anode and cathode solutions which have to be corrected for the weight of gas evolved during electrolysis as calculated from the coulometer readings. The total resistance of this apparatus varied from 10,000 to 100,000 ohms and the current from 0.01 to 0.04 amperes.

For very dilute solutions an apparatus of greater cross section made of boro-silicate glass one inch in diameter and consisting of two U-tubes ground together through side pieces was used. The analyses were checked by means of the Zeiss Dipping Refractometer. All vessels, instruments and solutions were carefully standardised before use. The chemicals used were Kahlbaum's best[1]. Several samples of oleic acid were used and their titration values frequently tested since it has been found by experience that even the best oleic acid oxidises on keeping. In these cases when the value was high the acid was thoroughly washed with frequent changes of water and dried in a vacuum dessicator over calcium chloride. If the molecular weight was then found correct the iodine value was not taken in view of previous work.

Solutions were made from sodium drippings and from conductivity water which had been boiled out in pyrex glassware. Medicinal white vaseline was boiled out with four changes of conductivity water and dried before use. Soap solutions were made up in Jena bottles by the direct neutralisation method of Bunbury and Martin[2]. Concentrations are expressed in weight normalities, that is, gram molecules of salt per 1000 grams of water.

Method of Analysis of Soap Solution

To a weighed quantity of solution contained in a stoppered flask a measured excess of standard hydrochloric acid was added slowly from a pipette with vigorous stirring. The precipitated fatty acid is allowed to stand overnight for the resulting emulsion to clear and then filtered off through wetted filter paper and washed free from hydrochloric acid with boiled out distilled water. The filtrate is titrated with standard sodium hydroxide using phenolphthalein, the difference between this and the amount of hydrochloric acid originally taken determines the total concentration of soap and hydroxide. The fatty acid in the filter paper is dissolved in boiled out alcohol and titrated with sodium hydroxide, which had been standardised both against the oleic acid used, and hydrochloric acid[3]. The solvent at the end point is made to be between 70 and 80 per cent boiled out alcohol.

Method of Calculating Results

To the weight of anode or cathode is added the weight of oxygen or hydrogen in grams equivalent to the silver deposited. From this is subtracted the weight of all glass ware, the sodium sulphate solution, the sodium found (calculated as metal) and the oleate as acid radicle. This leaves the weight of water which must have been introduced as soap solution before the experiment. From the original concentration of soap, the sodium oleate corresponding to this amount of water is calculated. The change in sodium and change in oleate expressed in equivalents, divided by equivalents of silver give the migration number of sodium and oleate respectively.

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[1] See Laing and McBain: J. Chem. Soc., **117**, 1507 (1920).

[2] J. Chem. Soc., **105**, 417 (1914).

[3] Hulett and Bonner: J. Am. Chem. Soc., **31**, 345 (1909).

Migration Data for Sols of Sodium Oleate

Tables I, II, III and IV contain the complete migration data for various concentrations of soap, Table I for soaps of concentration approximately 0.6N_w, Table II for those of approximately 0.5N_w strength, Table III data for approximately 0.4N_w and Table IV for approximately 0.2N_w soap. Table V contains the data for experiments with two much more dilute solutions of soap, carried out in order to observe the transition to crystalloid.

TABLE I

Transference Data for 0.5925N_w Sodium Oleate Solutions

Portion.	Equivalents change.		Transference number (n)		
	Na analysis.	Ol analysis.	Na analysis.	Ol analysis	Mean
Anode	+0.166	+1.100	−0.003	+1.115	
AM	+0.052	+0.003			
AMM	−0.221	+0.012			
MM	+0.013	+0.013			1.026
CMM	−0.004	−0.035	+0.064	−1.054	
CM	−0.032	−0.053			
Cathode	+0.100	−0.966			

Expt. 14, 80 volts, 15 milliamps., 4 hours, 21.5°C.
Silver deposit 0.0980 grams, sulphate strength = 2.5%.

TABLE II

Transference Data for 0.0145N_w Sodium Oleate Solutions

Portion.	Equivalents change.		Transference number (n)		
	Na analysis.	Ol analysis.	Na analysis.	Ol analysis.	Mean
Anode	+0.075	+1.188	+0.089	+1.190	
AM	+0.010	+0.006			
AMM	+0.004	−0.004			
MM	−0.003	−0.000			1.252
CMM	−0.010	+0.013	−0.325	−1.405	
CM	−0.013	+0.022			
Cathode	−0.302	−1.440			

Expt. 18, 500 volts, 32-34 milliamps., 1 hour, 17.5°C.
Silver deposit 0.1362 grams, sulphate strength = 5%.

Anode	+0.054	+0.929	+0.180	+1.043	
AM	+0.011	+0.026			
AMM	+0.039	+0.014			
MM	+0.076	+0.072			1.046
CMM	+0.006	−0.011			
CM	+0.007	+0.010	−0.054	−0.908	
Cathode	−0.061	−0.918			

Expt. 19, 80 volts, 4-5 milliamps., 4 1/2 hours, 17.5°C.
Silver deposit 0.1061 gms., sulphate strength = 5%.

(Table II continued on page 683)

(Table II continued from page 682)

Anode	+0.028	−1.069	+0.044	+1.069	
AM	+0.016	+0.011			
AMM	−0.004	−0.011			
MM	+0.010	−0.009	−0.042	−1.047	1.050
CMM	+0.018	+0.007			
CM	−0.065	−0.073			
Cathode	−0.005	−0.970			

Expt. 22, 500 volts, 38-42 milliamps., 1 1/2 hours, 18.5°C.
Silver deposit 0.2410 gms., sulphate strength = 5%.

Anode	+0.030	+1.045	+0.030	+1.045	
AM	−0.017	±0.000			
AMM	−0.010	−0.013	−0.002	−1.006	
MM	−0.028	−0.040			1.022
CMM	−0.040	−0.034			
CM	−0.302	−0.330			
Cathode	+0.395	−0.591			

Expt. 23, 500 volts, 50 milliamps., 1 1/2 hours, 19.5°C.
Silver deposit 0.2732 gms., sulphate strength = 5%.

TABLE III

Transference Data for $0.3970N_w$ Sodium Oleate Solutions

Portion.	Equivalents change.		Transference number (n)		
	Na analysis.	Ol analysis.	Na analysis.	Ol analysis.	Mean
Anode	+0.112	+1.070	+0.103	+1.054	
AM	−0.009	−0.016			
AMM	−0.005	−0.021			
MM	−0.075	−0.075	−0.090	−1.106	1.088
CMM	−0.051	−0.057			
CM	−0.391	−0.413			
Cathode	+0.417	−0.561			

Expt. 34, 500 volts, 26.33 milliamps., 2 hours, 10°C.
Silver deposit 0.2317 grams, sulphate strength = 3%.

Anode	+0.182	+1.241	+0.122	+1.133	
AM	−0.035	−0.036			
AMM	−0.025	−0.072			
MM	−0.007	−0.021			1.142
CMM	+0.010	−0.029*	−0.150	−1.162	
CM	−0.010	−0.079			
Cathode	−0.115	−1.083			

Expt. 36, 500 volts, 12-14 milliamps., 54 minutes, 5°C.
Silver deposit 0.04795 gms., sulphate strength = 3%.

*Some spilled, if 0.25 ccs. this = nil.

TABLE IV

Transference Data for 0.1990N_w Sodium Oleate Solutions

Portion.	Equivalents change.		Transference number (n)		
	Na analysis.	Ol analysis.	Na analysis.	Ol analysis.	Mean
Anode	+0.730	+1.622	+0.218	+1.233	1.201
AM	−0.512	−0.389			
AMM	−0.024	−0.033			
MM	−0.130	−0.147	−0.211	−1.144	
CMM	+0.221	+0.264			
CM	−0.676	−0.703			
Cathode	+0.374	−0.538			

Expt. 26, 500 volts, 11-14 milliamps., 1 1/2 hours, 19°C.
Silver deposit 0.0746 gms., sulphate strength = 3% (anhydrous).

Anode	+0.944	+1.756	+0.267	+1.212	1.143
AM	−0.677	−0.544			
AMM	−0.043	−0.079			
MM	−0.172	−0.168	−0.045	−1.049	
CMM	−0.026	−0.074			
CM	−0.344	−0.384			
Cathode	+0.397	−0.423			

Expt. 27, 500 volts, 12-14 milliamps., 1 1/2 hours, 19 7°C.
Silver deposit 0.1008 gms., sulphate strength = 3%.

Anode	+0.884	+1.684	+0.312	+1.351	1.326
AM	−0.492	−0.292			
AMM	−0.080	−0.041			
MM	−0.027	−0.025	−0.381	−1.262	
CMM	−0.214	−0.089			
CM	−0.118	−0.132			
Cathode	−0.049	−1.041			

Expt. 30, 500 volts, 12-15 milliamps., 1 1/2 hours, 21.5°C.
Silver deposit 0.0864 gms., sulphate strength = 3%.

TABLE V

Transference Data for Dilute Solutions of Sodium Oleate

Portion	Equivalents change.		Transference number (n)		
	Na analysis.	Ol analysis.	Na analysis.	Ol analysis	Mean
Anode	+0.28	+1.29	+0.28	+1.29	
AM	(+0.02	+0.06)	+0.02	+0.06	
AMM	−0.14	−0.13			
MM	−0.29	−0.24			1.225
CMM	−0.14	−0.11	−0.25	−1.09	
CM	−0.14	−0.12			
Cathode	+0.46	−0.49			
Concentration $0.048N_w$, 500 volts, 4 milliamps., 3 hours, silver deposit 0.0469 gms., sulphate strength = 3%, 20.5°C.					
Anode	+0.44	+0.57	−0.44	+0.57	
Middle	−0.14	−0.14			±0.58
Cathode	+0.58	−0.46	+0.44	−0.59	

Concentration $0.00985N_w$, 500 volts, 20 milliamps., (1 hour), silver deposit 0.0713 grams, sulphate strength = 5%, 20°C.

Apparatus employed for Gels and Curds. (See Fig. 2).

Preliminary experiments were carried out with w-shaped tubes. At first these were divided into anode and cathode compartments after an experiment

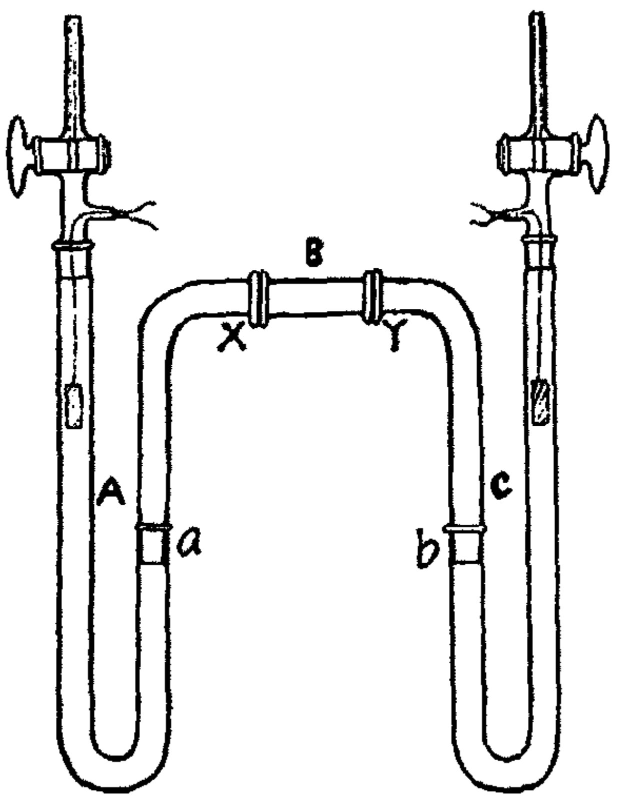

FIG. 2
Scale about 1:3

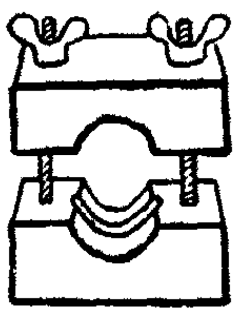

FIG. 2a.

by cutting through the glass at the centre of the bend. This was not convenient for filling, as the soap contaminated both limbs during the process. Some experiments were next carried out with an apparatus somewhat similar to Fig. 2 but connected with rubber tubing which was cut in the middle of the bend at the end of an experiment.

The final form of apparatus is shown in Fig. 2, where ground in stoppers replace the rubber and two Guye joints (Fig. 2a) (or sometimes one) between ground butt end tubes serves to hold both limbs together and to permit the curd or gel to be cut through with silver wire at the flat ground joint. The total resistance of this form of apparatus was from 30,000 to 250,000 ohms, the lowest silver deposit being 470 milligrams. In almost every case a sample of the soap gel or curd was taken at the cut to test for the presence of guard solution. In some cases if the migration was long protracted this removal of soap will account for slight disagreement between the two electrode portions although there is always agreement between constituents in each compartment. The test for sulphate was negative in all recorded experiments. Four semi quantitative preliminary experiments are not included owing to undue shrinkage of gel, which allowed sulphate to creep round into the middle portion.

To fill the apparatus the middle U-tube is inverted and filled with fluid soap solution. This is then placed in ice water to solidify the soap as curd. To transform it to jelly it is carefully warmed to 22° until it is clear of all curd fibres and yet does not flow on tilting. The state of the soap is again checked at the end of the experiment, when it is being cut through.

Alternative procedures were adopted depending upon whether the guard solutions of sodium sulphate were placed in direct contact with the solidified soap or a soap sol of the same concentration was interposed. When the first way was followed, the guard solutions were weighed in from a pyknometer and the air was readily removed by rotating the electrode tubes at right angles and then suitably tilting them. The second procedure had the advantage that if the jelly shrank during the experiment only soap sol and not guard solution could creep round the column of jelly.

In most experiments the gel showed considerable movement on the anode side, the boundary meniscus being often somewhat broken, while on the cathode, side the jelly usually adhered firmly to the side of the tube. If the jelly remained stationary throughout, liquid moved through it (electroösmosis), if not firmly fixed to the sides the jelly moved (electrophoresis).

Data for Migration of Electrophoresis in Soap Jellies

Tables VI to VIII contain data for the electrical migration in sodium oleate jellies. Table VI refers to soaps between the concentrations $0.5N_w$ and $0.6N_w$, Table VII gives data for soaps of approximately $0.4N_w$ and Table VIII refers to soaps of approximately $0.2N_w$ concentration.

TABLE VI

Transference Data for Transparent Jellies of Sodium Oleate, $0.5N_w$ to $0.6N_w$.

Concn. N_w,	Temp. °C	Grams silver	Portion.	Transference number (n). Na analysis.	Ol analysis.	Mean.
0.5145	20	0.1475	Anode	(−0.47)	+1.130	1.08
			Cathode	−0.075	−1.048	
0.5146	20*	0.1616	Anode	+0.002	+0.978	1.01
			Cathode	−0.037	−1.024	
0.5240	16	0.0498	Anode	+0.23	+1.29	1.19
			Cathode	−0.14	−0.10	
0.5240	16	0.0503	Anode	(−0.12)	(+0.90)**	1.01
			Cathode	−0.04	−0.98	
0.6177	16	0.1364	Anode	(−0.35)	(+0.70)	1.07
			Cathode	−0.048	−1.092	

80 volts, 120-150 mins., 5-16 milliamps., sulphate strength = 5% in first two experiments, 2.5% in others.

*Temperature raised to 24° for short period during experiment to prevent curding.
**Ether extraction, therefore inaccurate.

TABLE VII

Transference Data for Transparent Jellies of Sodium Oleate, Concentration approximately $0.4N_w$.

Concn. N_w	Temp. °C	Grams silver	Portion.	Transference number (n). Na analysis.	Ol analysis.	Mean.
0.3861	Room	0.1112	Anode	—	—	1.055
			Cathode	−0.049	−1.042	
0.3912	17.5	0.0206	Anode	−0.14	+0.98	0.96
			Cathode	(−0.11	+0.95)	
0.3912	17	0.01895	Anode	+0.09	+1.11	1.105
			Cathode	−0.10	−1.12	

80 volts, 140 mins., 2-10 milliamps., sulphate strength = 2.5% in first experiment 1% in others.

TABLE VIII

Transference Data for Sodium Oleate Gels. Concentration $0.2N_w$ (approx).

Conc. N_w	Temp. °C	Grams silver	Portion.	Transference number (n). Na analysis.	Ol analysis.	Mean.
0.1990	22	0.0526	Anode	+0.105	+1.174	1.185
			Cathode	−0.230	−1.212	
0.1990	22	0.0636	Anode	+0.049	+1.150	1.095
			Cathode	(−0.34?	−1.187)	

30 to 34 milliamps., 500 volts, 30 mins., sulphate strength = 3%.

Electrical Migration or Electroosmosis in Soap Curds

Tables IX to XIII contain results obtained by the electrolysis of sodium oleate curds, of the concentration range as before, $0.2N_w$ to $0.6N_w$.

TABLE IX

Transference Data for 0.5959 Sodium Oleate Curd

Temp. °C	Grams silver	Portion.	Transference number (n). Na analysis.	Ol analysis.	Mean.
10	0.0732	Anode	+3.33	+4.37	
		Middle	+0.08	+0.16	4.49
		Cathode	−3.88	−4.71	

500 volts, 6-18 milliamps., 110 mins., sulphate strength = 5%.

TABLE X

Transference Data for $0.5258N_w$ Sodium Oleate Curds

Temp. °C	Grams silver	Portion.	Transference number (n). Na analysis.	Ol analysis.	Mean.
16	0.0410	Anode	+0.748	+1.973	1.770
		Cathode	—	—	
16	0.1299	Anode	+0.325	+1.276	1.460
		Cathode	−0.625	−1.616	
16	0.128	Anode	+0.560	+1.537	1.519
		Cathode	−0.505	−1.473	
16	0.1148	Anode	+0.825	+1.790	1.847
		Cathode	−0.912	−1.861	
16 *	0.1029	Anode	+1.498	+2.471	1.454
		Cathode	−1.430	−2.421	

80 volts, 120-160 mins., 8-10 milliamps., sulphate strength = 5%.

*Concentration 0.5145Nw.

TABLE XI

Transference Data for Sodium Oleate Curds 0.3970N_w

Temp. °C	Age (days)	Grams silver.	Portion	Transference number (n). Na analysis.	Transference number (n). Ol analysis.	Mean.
0	105	0.0623	Anode	+3.294	+4.293	4.27
			Cathode	−3.233	+4.283	
5	12	0.0479	Anode	+3.980	+4.986	4.98
			Cathode	−3.994	−4.984	
10	26	0.0483	Anode	+4.19	+5.29	5.27
			Cathode	−4.42	−5.46	
18	8	0.1495	Anode	—	—	2.11
			Cathode	−1.133	−2.079	

500 volts, 54-105 mins., 12-25 milliamps., sulphate strength = 5%.

TABLE XII

Transference Data for 0.366N_w Sodium Oleate Curd.

Temp. °C	Age (days)	Grams silver.	Portion.	Transference number (n). Na analysis.	Transference number (n). Ol analysis.	Mean.
10	27	0.0492	Anode	+3.362	+4.235	4.40
			Middle	−0.012	−0.017	
			Cathode	−3.416	+4.472	

6-10 milliamps., 500 volts, 80 mins., sulphate strength = 3%.

TABLE XIII

Transference Data for 0.1990N_w Sodium Oleate Curds

Temp. °C	Grams silver	Portion.	Transference number (n). Na analysis.	Transference number (n). Ol analysis.	Mean.
16	0.0411	Anode	(+0.459)	+1.534	1.61
		Cathode	−0.673	−1.639	
14	0.0574	Anode	+0.707	+1.703	1.71
		Cathode	(−1.352	−2.382)	

500 volts, 65-45 mins., 6-16 milliamps., sulphate strength = 5%

Discussion

The Inherent Identity of "Migration", "Electrophoresis" and Electroösmosis" in Solutions and Jellies of Soap

The movement of each constituent of soaps in solution relative to the solvent during the passage of the current is unaffected by gelatinisation and remains the same whether the jelly moves as a whole or in parts through the solvent or when the jelly is fixed so that the solvent has to move through the jelly.

It is evident that identity in their very nature exists between the three phenomena of migration, electrophoresis and electroösmosis and that they should therefore be treated from the same standpoint and not regarded as belonging to different branches of science.

The movement relative to the solvent in sols or jellies of sodium oleate which was given in detail in the previous tables is summarised in the following Table XIV, in terms of equivalents of fatty acid transported towards the anode per faraday of current. The movement of sodium is in necessary accordance with Faraday's law and in agreement with the measurements, one equivalent less in the same direction. The values for curds are given for comparison but they are governed by other experimental conditions.

Table XIV

Comparison of Observed Hittorf Transference Numbers for Sols and Jellies of Sodium Oleate

Concn. (N_w).	Sols	Jellies.	Curds.
0.6	1.05	1.07	4.49
0.5	1.09	1.07	1.69 to 2.45
0.4	1.12	1.08	2.11 to 5.27
0.2	1.22	1.19	1.61 to 1.71

Bearing upon Theory of the Structure of Jellies

In 1920 McBain and Laing pointed out the significance of the fact that sols and jellies of soap differ only in their mechanical properties and exhibit the same conductivity, osmotic behaviour, concentration of sodium ions, refractive index etc. To this must be added their identical behaviour during the passage of an electric current in spite of the enormous difference in elasticity and rigidity. Evidently the same equilibria and the same colloidal particles exist in sol and gel.

They pointed out that these facts preclude the existence of an emulsion structure such as that postulated by Wo. Ostwald and M. H. Fischer, or an open or closed honey comb structure such as that postulated by Bütschli, leaving only the possibility that the structural basis of the jelly is built up of the colloidal particles which have almost wholly retained their individuality like beads in a necklace. This is essentially a reversion to the micellar theory of Nägeli which has received much strong support from Zsigmondy, Pauli, Bachmann, and recently Bogue.

There are various ways in which colloidal particles can be put together so as not to interfere with the conductivity of the solution, such as in filaments, or "brush heap" (Holmes) or even by assuming that the micelles are themselves chains of single molecules. Experiment has not yet decided between these variants of micellar structure, but it has to be remembered that in soap solutions the conductivity is largely due to the minute ionic micelles[1] whereas the gel structure is probably built up from the much larger particles of neutral colloid. For purposes of measurement with alternating current the ionic micelles appear to move as readily through a soap jelly as through the same solution when fluid, but during prolonged electrolysis with direct current ocular observation appears to afford evidence of strain and of tearing of jellies of soap and gelatine. This point will be considered again.

Curds are wholly different from sols and gels in that a process analogous to crystallisation has occurred with the separation from solution of hydrated neutral soap in the form of white fibres[2] whose X-ray structure has been investigated by my colleague Mr. S. H. Piper[3] whereas sols and gel exhibit no such structure. These fibres enmesh a mother liquor which is saturated with respect to them and whose concentration may be determined by analysis, lowering of vapour pressure and diminished conductivity.

Possible Alternate Explanation of Electroösmosis

There is but one current explanation, namely the Helmholtz double layer but we can here suggest three further mutually exclusive alternative mechanisms to explain cataphoresis and endosmosis, only one of which is in accordance with the facts here presented.

1. The Helmholtz double layer as currently accepted may be made to harmonise with any conceivable set of facts and is therefore useless as a working hypothesis.

2. There seemed to be a possibility that in electroösmosis there might be found a method of measuring the hydration of a simple ion, whereas the classical experiments of Washburn and others merely measure the difference between hydrate water carried by cation and anion. The hypothesis is that in electroösmosis neither diaphragm nor solvent as such moves with respect to the electrodes. The apparent movement would then be attributed to the hydrate water carried by the free ions of opposite sign to the charges on the diaphragm. In the present case, the ions in question would have to be hydrated sodium ions carrying water towards the cathode and the rigid surface would be represented by curd fibres or the particles of neutral colloid, not included in the ionic micelle. This leads to a direct numerical prediction which is not in accordance with the experiments as will be shown in the general discussion on the influence of hydration in a later section.

3. It is recognised that during the electrolysis of any ordinary electrolyte tremendous forces are being applied to move the ions through the solution with appreciable velocity and that anion and cation exactly adjust their velocity so that they are in inverse proportion to the forces required to overcome the frictional resistance or drag, leaving thus no residual hydrostatic pressure on the solution in either direction. It may be that in the outer mo-

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[1] McBain and Jenkins: J. Chem. Soc., **121**, 2325 (1922); Bowden; J. Chem. Soc., **123**, 2417, (1923), and later.

[2] McBain and Laing: J. Chem. Soc., **117**, 1507 (1920).

[3] Proc. Phys. Soc. Lond., **35**, 269 (1923).

bile layer of free ions this great frictional effect would persist but not be compensated by any comparable frictional resistance of the rigid surface. In this case the whole of the solution would move bodily with the free ions past the charged surface. This again leads to a definite but different numerical prediction which is not in accordance with the facts (see below). It is also very similar to the description given by Burton that the solution is bodily dragged through as it were by its skin.

4. It seems probable that the correct view is that, in all systems, positively and negatively charged carriers and materials, whether ions, colloidal particles or surfaces, exhibit frictional resistance or drag of the same order of magnitude, (although of course not equal) and that their treatment should be exactly like that accorded to any ordinary electrolyte. This underlies the observation of Müller referred to in the introduction, and finds quantitative expression in the general formula developed in this paper.

The difficulty which stands in the way of hypothesis (2) may be briefly summarised, in order to show that this suggestion must be dismissed. Various sets of arbitrary assumptions may be made to see if by any possibility the data here presented may be made to fit the hypothesis. For instance, one may take the true migration number predicted for the ionic micelle from conductivity data as 0.60, with the assumption that the whole of the neutral colloid is included in the ionic micelle. In any case since the total colloid is five times greater than the aggregated oleate ions, a true movement of 0.6 of ionic micelle ought to yield an apparent migration of $5 \times 0.60 = 3.0$ equivalents of oleate radicle moving to the anode. Any hydration of the sodium ion would simply magnify this and bring it further away from the observed value of 1.08 so that hypothesis (2) is in the wrong direction.

Again if it is assumed that the ionic micelle is quite free from neutral colloid, there is a discrepancy of from 1.08 to 0.00 between observed and predicted values which would be accounted for if the hydration of the sodium ion is $(Na + 132H_2O)$ in N/10 solution of sodium ion, with the hydration increasing in nearly direct proportion to the dilution. This is an absurd hydration to ascribe to the ordinary sodium ion. It is particularly so in view of the previous experimental proof of McBain and Jenkins that it is the *soap* that is exceptionally hydrated.

Another compromise might be effected by assuming just enough neutral colloid in the ionic micelle to fit in with any hydration of the sodium ion from 0 to the value just given, but even this final possibility disappears when we compare the results for sol and gel with the much higher values of curd or the same total concentration.

If the sodium ion is taken as having a constant hydration, curd ought to have given the same migration as sol and gel instead of being several times greater, whereas if the hydration of sodium ion is taken as being proportional to the dilution it can just be made to explain a few cases of the observed curds but is then several fold in error for the remainder.

Hypothesis (2) is thus irreconcilable with the experimental facts.

Hypothesis (3), which is to the effect that the sodium ion carries the whole of the mother liquor bodily with it past the colloid, predicts a migration number of about 5.0 (because there are 5 equivalents of soap in the amount of solution containing one equivalent of Na.) if expressed in terms of oleate radicle, whereas the value observed is only a small fraction of this, namely 1.08.

It might have been possible partially to adopt the suggestion of hypothesis (3) but only by speculating that the movement of the particles of ionic micelle is of a different character from the movement of particles of neutral colloid and allowing it only to explain the electrophoresis of the latter but not of the former in the same solution. Even so, this is found to lead to an electric charge on the neutral colloid which is at least 1/8 as great as that of the ionic micelle and which may even exceed it. Further, the same incompatibility between the results for curd and sol is met with as in hypothesis (2).

It is thus seen that the only standpoint from which all the data can be consistently maintained is that of electrolytic migration that is, hypothesis 4) as explained in the introduction and embraced in our quantitative formation.

The Reason for the High Value of the Apparent Migration Number of Sodium Oleate

The transport number of an ordinary sodium salt of a heavy organic acid is 0.32. The lowest value found in any case is 0.58 for $0.01N_w$ sodium oleate solution (Table V). There is still an appreciable amount of colloid in solution even as dilute as $0.04N_w$. In higher concentrations the experimental value exceeds unity in sol and gel and the sodium moves on the whole towards the anode. The curd presents the same behaviour in highly exaggerated form.

It will be shown that the high values are due not merely to high mobility of the ionic micelle with its aggregated oleate ions but that the undissociated colloid also moves independently although more slowly towards the anode, the two together thus carrying more sodium towards the anode than is carried through the migration of sodium ions towards the cathode.

In $0.01N_w$ solution, although the soap is crystalloidal (apart from small quantities of colloidal acid soap) the apparent migration of the sodium is only 0.42 because an appreciable fraction is being carried by the small amount of highly conducting sodium hydroxide formed by hydrolysis. The quantitative calculation from the concentrations shown in the diagram (Fig. 3) predicts that the movement of the sodium ion under these conditions should have been 0.43 since the movement of soleate ion is 0.28 and that of hydroxyl ion 0.29. The method of analysis does not distinguish between these two but gives their sum and although no stress can be laid upon an obviously inexact experiment, the mean result coincides with that predicted.

Formulae for calculating the Effects of Hydration upon Apparent Migration

McBain and Salmon[1] were unable to decide with regard to the constitution of the ionic micelle as to whether it consisted solely of aggregated and hydrated fatty ions or whether it contained as well some or all of the neutral colloid.

Bowden has pointed out that his migration results seem to show that the neutral colloid was mostly independent of the ionic micelle, and very direct evidence to the same effect was obtained by McBain and Jenkins in ultrafiltration. However it is worth while scrutinising the present results to see whether the same conclusion inevitably follows.

In the first place if the whole of the colloid were assumed to be in the ionic micelle, the migration number ought to have been 3.00 instead of 1.08 and the only way of reconciling the two results is by assuming excessive hydration of the ionic micelle, resulting in the apparent bodily displacement of the whole solution towards the cathode.

The following is the formula for calculating the magnitude of such effects of hydration. For each unit of discrepancy between the apparent and true migration number there has to be carried by one equivalent of the anion a litre, or 1000 grams or 55 mols of water, divided by the product of the total normality of the solution and the true migration number, that is, one equivalent of the anion must be combined with

$$\frac{55\,v}{n} \text{ mols of water}$$

where v = number of litres of solvent containing one mol of solute. The total water in the solution is only 55v so that at first sight it would seem that one unit discrepancy of the migration number would require several times as much water of hydration as the solution contains and it might seem that hydration never could cause anything like a unit discrepancy even of the whole of the water in solution were taken as combined with one of the ions leaving no solvent. However, this would only be true for one hundred per cent ionisation, whereas for incompletely dissociated substances at any given moment the amount of water combined with the amount of ion actually present would be

$$a \cdot \frac{55\,v}{n}$$

In the case of the more concentrated solutions of sodium oleate a is only 20% in terms of the Arrhenius theory.

Attempting to apply this formula to $0.5N_w$ sodium oleate where the discrepancy is 3.00 minus 1.08 = 1.92 units, 352 mols of water would be carried per one electrochemical equivalent of micelle, therefore the water carried by the micelle as hydrate water would have to be 72 mols of water to 1 mol micelle, but the total water present is only 110 mols, therefore the value indicates that 2/3 the total water present would have to be water of hydration of ionic micelle. (The same values of predicted hydrate water may be arrived

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[1] J. Am. Chem. Soc., 42, 426 (1920).

at by use of McBain's more general formula[1] where the difference in migration number due to hydration is expressed as $(u\alpha - v\beta)c$ where α and β are the number of water mols combined with cation and anion and c is the concentration of the solution in equivalents per 18 cc.) It is also seen that this hydration must be taken as being practically proportional to the dilution, that is 2/3 the total water for such concentration of sodium oleate would have to be regarded as hydrate water.

It is obvious that these values are far too high to be considered and that we must reject them entirely. (Reference might have been made to Barratt and Harris[2] who though favouring the hydration theory of ions of hypothesis (2) were overwhelmed by its consequences, for they calculated that anywhere between 18 and 370 mols of water were transported through agar diaphragms for every molecule of solute decomposed electrolytically). It is much more reasonable to assume that the hydration of the ionic micelle is at least approximately constant.

It is necessary then to assume that much of the neutral colloid exists and moves independently of the ionic micelle, a conclusion which will be strengthened in the following paragraphs.

The Change in Migration Number with Concentration

Before carrying out further calculation it is well to recall the results obtained by Bowden who observed a small but definite decrease in migration number in high as compared with medium concentrations. The same thing has been found in the present case. For convenience these results are summarised in the following table.

TABLE XV

Effect of Concentration on Migration Numbers

Transference number.	$1.0N_w$	$0.5N_w$	$0.2N_w$	
NaOl sol		1.086	1.204	Laing
NaOl gel		1.086	1.182	
K laurate	0.55		0.67	Bowden
K oleate		0.70	(0.25N) 0.75	

We shall explain this change of migration number with concentration as being due to hydration since from the formula already given it is seen that a hydration exerts an effect which is approximately proportional to the concentration. Before doing so, a word may be said with regard to current alternative methods of explaining change of migration number with change of concentration. Our opinion is that when such change is observed in very dilute solution, as is the case of hydrochloric acid, it is because change of conductivity affects the actual hydration of the two ions unequally (which is in accordance with the mass law) that is, the effect is due to change in the actual formula and properties of the ion.

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[1] Z. Elektrochemie, 14, 216 (1905).

[2] Z. Elektrochemie, 18, 221 (1912).

There are two other general methods of explaining the change of transference ratios with concentration, the formation of complexes and the change in viscosity of the medium. Since we can evaluate the constituents of soap solutions we need not invent other complexes and we can put aside the viscosity correction of transport numbers after consideration of our results for sol and gel. Here an enormous increase in viscosity in changing from fluid sol to rigid gel does not lower our migration number, or even the conductivity, in the slightest degree. The change in migration number with concentration cannot then be due to change in viscosity. This seems to show too that the attempt to explain anomalous conductivity by change of viscosity is of doubtful value. In any case it is remarkable that the attempt should be made to explain migration by change in viscosity of the medium which presumably should affect all ions alike.

Distinction between Neutral Colloid and Ionic Micelle of Sodium Oleate Sols and Jellies

If hydration is to explain the change of transport number with concentration we can calculate that most of the neutral colloid is not contained in the ionic micelle but also exists separately from it and we can also deduce the total movement of this undissociated soap during the passage of the electric current.

We proceed by assuming an approximately constant hydration for the concentrations $0.5N_w$ and $0.2N_w$ for which the migration numbers 1.08 and 1.20 are observed. If we take it that there is enough neutral colloid so that apart from the effect of hydration the apparent migration number would be raised from the true value 0.60 to 1.28 in both cases, the hydration which would bring this to the experimentally observed migration values is 35 mols of water per equivalent of micelle and the neutral colloid moving simultaneously with the micelle is $\frac{1.28-0.60}{0.60} = 1.13$ equivalents per equivalent of ionic micelle.

It is obvious that this definite result may be expressed in either of two ways, the first suggestion is to put all these constituents into the ionic micelle whose formula would then be (Ol′ 1.13 NaOl, 35 H_2O)x. The remainder of the neutral colloid, nearly 3/4 of the whole, would in this event have to be regarded as being free and independent and completely uncharged and since it would not be moved with the electric current its own hydration would not come into account, although we would have to admit that it was passively displaced towards the cathode by the 35 mols of water carried with the ionic micelle towards the anode. It is more rational to account for the same total movement of these three constituents by a different allocation between ionic micelle and neutral colloid, the great difference between the two views being that when neutral colloid is in the ionic micelle it must move as fast as the ionic micelle whereas the same total movement is obtained by ascribing a correspondingly slower movement to the whole of the neutral colloid if moving independently of the ionic micelle.

Although it is an extreme view to regard the ionic micelle as containing no neutral colloid at all, yet since it has been shown that most of the neutral colloid is in any case independent of the ionic micelle, further results will be discussed upon this basis as a useful approximation to the truth and it will be seen that thereby the whole of our results even with curds can be quantitatively accounted for.

The movement of 1.13 equivalents of sodium oleate to each equivalent of oleate must now be distributed over the whole of the neutral colloid and since the neutral colloid present is in the proportion of 1 to 4 micelle, it must now be taken as moving $\frac{1.13}{4}$ times as fast. It will be shown below that this factor $\frac{1.13}{4}$ suffices for the prediction of the effective mobility of the curd fibres which are likewise composed of neutral colloid.

Further experiments on ultrafiltration will decide as to the allocation of the 35 mols of water as between ionic micelle and neutral colloid but in any case 35 mols of water accompany the movement of one equivalent of polymerised oleate ions and that of four equivalents of sodium oleate making a mean value of 7 mols of water to one equivalent of oleate radicle.

This estimated hydration can be further altered only by taking into account the possible hydration of the sodium ions also. Inserting Washburn's value of $Na^{\cdot}10H_2O$, and using McBain's formula for the total correction due to hydration

$$(u\alpha - v\beta)c$$

the total 35 mols of water moved towards the anode per equivalent of micelle becomes nearly 42 mols water, and taking into account the degree of dissociation this would require 8.4 mols actually present at any one time. With the 2.0 mols in the corresponding ions we therefore arrive at a value 10 mols of water per equivalent of total soap. The net movement of neutral colloid is unaffected and remains as before 1.13 equivalents per equivalent of ionic micelle and its effective mean mobility $\frac{1.13}{4} = 2/7$ of that of the ionic micelle. It is thus seen that the effective mobility or f_1 of the ionic micelle in terms of our general formula, is nearly equal to f_1 since one electrical charge has been assumed for each oleate radicle. On the other hand although the effective mobility m_2f_2 of the neutral colloid amounts to as much as 2/7 of that of the ionic micelle, nevertheless it is probable that this is merely due to the enormous value of m_2, the number of chemical equivalents required to carry one electrical charge. An attempt will be made in a further investigation to evaluate m_2f_2 separately and we expect to procure measurements of the equivalent conductivity of neutral colloid and curd fibres as well as the mechanical obstruction which they offer to the passage of the electric current.

Corresponding Recalculation of McBain and Bowden's[1] Value for Potassium Oleate and Potassium Laurate

We can now establish the values required to explain the migration data for potassium oleate and potassium laurate in various concentrations. We get the strikingly simple result that the behaviour of potassium oleate is quantitatively predicted if we assume the same effective mobilities for ionic micelle and for undissociated colloid as we have found in the case of our sodium salt. Their data therefore corroborate the conclusion that the ionic micelle contains very little soap and that the effective mobility of the undissociated colloid is 0.34 times that of the ionic micelle. The effective mobility of undissociated colloid in potassium laurate is distinctly higher, namely 0.51. Details of these calculations now follow.

Potassium oleate may be taken as being 30% dissociated into ionic micelle and 70% neutral colloid. The migration numbers observed for 0.5 were 0.70 and 0.75 respectively. To give the ionic micelle approximately the same percentages composition in both solutions, it is found necessary to assume that the hydration is about 23 mols of water per equivalent of ionic micelle, and correcting for the hydration of the potassium ion ($6H_2O$), this becomes 29.3 mols of water. The corresponding amount of neutral colloid in one equivalent is 0.78 equivalents for each one equivalent of ionic micelle, the relative amounts being 30% and 70%. The relative rate for equal quantities of neutral colloid and ionic micelle are in the proportion of 0.34 to 1, exactly the same result as we have with sodium. Ultrafiltration has not yet been employed to check this value for the hydration of the potassium salt.

The calculation for the laurate is slightly more laborious because account has to be taken of the simple laurate ion which is present in appreciable amount in dilute solutions. The observed migration values in 1.0 and 0.2N K laurate are respectively 0.55 and 0.67 from which it follows that the hydration water moved for each equivalent of ionic micelle is 35 mols of water, and, correcting for the hydration of potassium, this becomes 41 mols of water, the neutral colloid then being 0.88. Taking into account the relative proportions of neutral colloid and ionic micelle present, each equivalent of neutral colloid is moving 0.51 times as fast as an equivalent of ionic micelle. It might be noted however that if Bowden's result for 0.2N potassium laurate solution had been very slightly lower this result and the hydration would have been appreciably lowered. The hydration found when spread over the total soap present is about 17 mols equivalent, whereas Jenkins found as a minimum about 12 mols of water.

The values adopted for the hydration are of the same order of magnitude as those which alone are consistent with the direct experimental measurements of the movement of glycerine in Bowden's electrolysis.

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[1] J. Chem. Soc. 123, 2417 (1923).

Discussion of Results for Soap Curds

Here again, the relative movement between the soap constituents and water is independent of whether the curd itself is free to move or fixed so that the water must move through it.

The soap curds show a range of migration values which may even exceed five equivalents carried towards the anode per faraday of current. Curds contain curd fibres of neutral colloid which has separated from the solution they enmesh. Examination of the results shows that the highest values of migration are obtained where the highest proportion of the soap is in the form of these fibres. Before evaluating the results it is necessary to establish the concentration of the mother liquor surrounding the curd fibres. Although more dilute, it is an ordinary soap solution containing ionic micelle, neutral colloid and sometimes simple oleate ion.

There are two methods of finding the relative amounts of mother liquor and curd fibres. The one suggested in the earlier paper was the use of conductivity measurements. Data are recorded (Laing and McBain[1]) which show the conductivity of these soaps whether as curd or sol. In each case the conductivity of the curd is lower than the sol and although it decreases as more fibres develop, it always remains an appreciable value. The drop in conductivity when fibres form may be attributed to the removal of some constituents from the solution, and ratio

$$\frac{\text{conductivity of curd} \times \text{concentration}}{\text{conductivity of sol}}$$

should give the number of equivalents remaining in solution (not as curd fibres). This however neglects any effects of the mechanical resistance of fibres as well as any residual conductivity which they may contribute.

The second method only recently tried should give results which are more comparable with the curd under investigation. A large conductivity cell of borosilicate glass as used in previous work[2] has been specially constructed so that the central portion of the column of glass ware between the electrodes can be bodily removed. This is easily done by the use of Guye joints and glass tubing with ground butt-ends as already described. The soap to be investigated, of the same concentration as one for which transference numbers are available is poured into the cell, whose cell constant has been determined with N/10 KCl, and allowed to curd. After a specified time (one week at 0° in the three experiments carried out) the conductivity of the curd is taken at the required temperature with the Leeds and Northrup conductivity set. The inset tube is then removed and at the same temperature the column of curd is compressed against a perforated porous plate and the few drops of mother liquor thus squeezed out are allowed to fall on the ground glass wedge of the Zeiss Dipping Refractometer. Their refractive index is then read and the concentration to which the value refers is taken from our standard graph.

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[1] J. Chem. Soc., 117, 1506 (1920).

[2] Laing and McBain: loc. cit.

This affords a very direct check on the former method and yields predicted values for migration which are very near those found. The calculation will now be described.

Application of our Theory in predicting the Migration Data for Soap Curds, with the effects of Temperature and Concentration

Knowing the concentration of mother liquor bathing the fibres we can read off its constituents[1] in percentages from Fig. 3. These can be expressed in terms of effective mobility by introduction of the conductivity values and concentration of each constituent. But the value so obtained is only a part of the migration number because we have omitted the curd fibres which constitute a large portion of the solution and which contribute to the total transference through electrophoresis of neutral colloid. Before calculating the total transference the concentration of curd fibres has to be added to the concentration of neutral colloid contained in the solution.

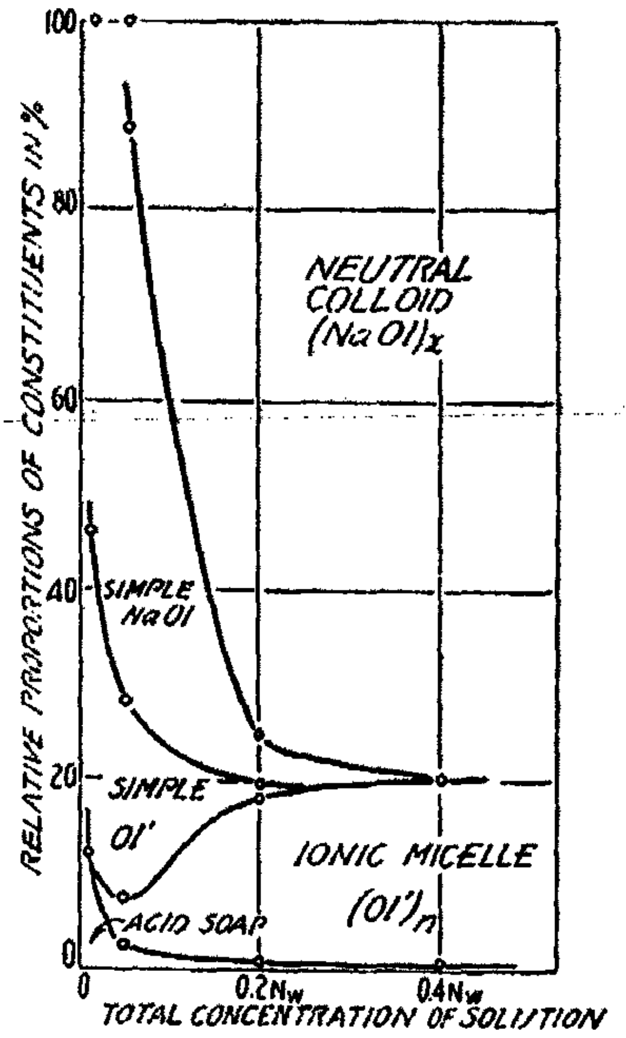

Fig. 3.

The relative proportions of the various constituents of solutions of pure sodium oleate at 18°c.

A specimen calculation of Expt. 21, is given to show how the predicted numbers are arrived at implicitly assuming the formula

$$n = \frac{'cv' + c_1m_1f_1 + c_2m_2f_2}{\mu}$$

and taking m_1 in the ionic micelle equal to unity and $m_2f_2/f_1 = 0.34$

$0.5145N_w$ soap curd is bathed by mother liquor of 0.239N.
0.239N solution reading from diagram (Fig. 3) consists of

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[1] The proportions of each of the constituents of solutions of sodium oleate have been determined from our previous osmotic and conductivity measurements by the method described by McBain, Laing and Taylor (J. Chem. Soc., 121, 628 (1922)), using Sherrill's formula (J. Am. Chem. Soc., 32, 741, (1910). Fig. 3 is a diagrammatic representation of the percentage composition of solutions of sodium oleate of concentrations $0.01N_W$ to $0.4N_W$ obtained in this way. The main constituents in concentrated solutions are colloidal, namely, ionic micelle and neutral colloid. The ionic micelle is a colloidal particle which is an aggregate of ordinary fatty ions such as oleate (Ol′) which have retained their electric charges so that the soap in the particles together with the corresponding sodium ions, exhibits an equivalent conductivity which is even greater than before aggregation. Its approximate formula would be $(Ol')_{10}(H_2O)_m$. Neutral colloid, is hydrated aggregates of undissociated soap with only a slight electric charge. The other conducting constituents are simple oleate ion, and sodium ion as dissociation products of sodium oleate salt. The percentage of Na ion is of course equal to the sum of the percentage amount of ionic micelle plus the percentage amount of the simple oleate ions. In addition in dilute solution there is a very small amount of acid soap and hydroxyl ions. The mobilities of the several ions at 18° were assumed to be Na. = 43.6 Cl′, = 20.7, ionic micelle = K. = 64.7, OH′ = 174.

Simple Ol′ 1%, ionic micelle 18.5%, neutral colloid 77%.
1% of 0.239 = 0.002, expressed as conductivity is $0.0024 \times 64.3 = 0.154$
18.5 of 0.239 = 0.044. expressed as conductivity is $0.044 \times 108.4 = 4.786$.
77% of 0.239 = 0.184 = 4.16 ionic micelle.
Therefore migration for substance in solution

$$\frac{4.786}{4.940} \times 0.60 \text{ for ionic micelle} = 0.581$$

$$\frac{0.154}{4.940} \times \frac{20.7}{64.3} \text{ for simple Ol}' = 0.010$$

$$\frac{1.13}{4} \times 4.16 \times 0.60 \text{ in neutral colloid particles} = 0.706$$

$$\text{Total} = 1.297$$

But taking the fibres into account
Concentration of fibres is 0.5145 − 0.239 = 0.2755 N.

$$\text{i.e. } \frac{0.276}{0.044} \times \text{ionic micelle} = 6.26$$

$$\text{i.e. for fibres } \frac{1.13}{4} \times 6.26 \times 0.60 = 1.011$$

Therefore total transference is 1.297 + 1.011
= 2.31 predicted.
= 2.45 found.

The values predicted for every curd are given in the final column of Table XVI and it is seen that they agree surprisingly well with the transference actually observed.[1]

TABLE XVI

Comparison of Predicted and Found Values for Curds using Formula x.

Total normality of soap.	Temp. °C	Normality of mother liquor.	Normality of curd fibres.	Migration numbers. Predicted.	Found.	Maximum divergence in migration nos.
0.556	10	0.165	0.391	4.03	4.40	—
0.5240	18	0.314	0.210	1.87	1.69	±0.18
0.5145	18	0.239	0.276	2.31	2.45	±0.03
0.3970*	0	0.087	0.310	4.37	4.25	±0.03
0.3970*	5	0.093	0.304	4.10	4.98	±0.00
0.3970	10	0.117	0.280	4.90	5.27	±0.13
0.3970	18	0.216	0.181	2.08	2.11	±0.02
0.366	10	0.168	0.198	4.40	4.40	±0.07
0.1990*	14	0.122	0.077	1.96	2.03	±0.34
0.1990*	16	0.130	0.069	1.60	1.61	±0.07

*Corrected for neutral particles in low concentration of mother liquor.

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[1] The one remaining item left out of the calculation of the curd is the effect of the movement of the hydrate water of the curd fibres, since they are not anhydrous. However a rough estimate shows that the predicted values for curd would be lessened by only a very few per cent at most.

It is well to remember that velocity of cataphoresis and mobility are not equivalent and should not be confused since the first is m_1 times the second. They are only identical if m_1 is equal to unity, that is, if there is one electrical charge per chemical equivalent. This confusion has for instance arisen in the literature of proteins where the total movement m_1f_1 has been interpreted as being ionic mobility f_1.

Low temperature and age each decrease the concentration of mother liquor and these effects are as pronounced as to furnish a searching comparison between theory and observation.

The agreement between prediction and experiment substantiates the formula developed in the present paper and justifies the simplification of the electroösmosis which enables us to express it in terms of conductivity and concentration.

Comparison with any good discussion of electrophoresis and electroösmosis on the hitherto accepted lines such as the excellent account given by Briggs in the Second Colloid Report makes it evident how much simpler is our present consistent standpoint of electrolytic migration. For instance, the most important effect of temperature is the alternation of viscosity which is known to condition the temperature coefficient of specific conductivity and hence also the amount of current produced by a given potential but all that matters is the total current that passes. Similar treatment applies to Burton's experiments on the electrophoresis of silver sols.

Visual Observation during Electrolysis

In most experiments on electrophoresis and electroösmosis of soap jellies and curds a layer of highly refracting liquid pushed forward towards the anode beyond the soap boundary making a clear mirror like surface where it came in contact with the sulphate solution. A few typical experiments are recorded in Table XVII.

TABLE XVII

Moving of Soap Boundaries during Electrolysis of Clear Jellies

Concn. N_w.	Time in mins.	Portion.	Movement in millimetres.	
			Jelly boundary	Clear layer beyond jelly.
0.53	90	Anode	+9	+4
		Cathode	none	none
0.51	60	Anode	+10	+6
		Cathode	−3	none
0.39	30	Anode	+6	+4
		Cathode	−2	none
0.39	60	Anode	+13	+2
		Cathode	−6	none

It is seen that the layer of clear liquid advances towards the anode distinctly faster than the body of the soap jelly itself, indicating a separation of the two constituents. In a simple case of a solution containing only one anion, we have no such separation. Thus when potassium permanganate is electrolysed between two colourless solutions the red colour moves bodily without developing any such irregularity . Here however we have the fast moving ionic micelle followed by the slower moving but larger amount of neutral colloid.

The presence of more than one carrier in the electroösmosis in clear jellies, whether of soap or gelatine, is often evidenced by the disintegration into discrete flocks which often progressively appear during the passage of the current. It must however be remembered that the jelly is fairly fragile and on the whole the structure of the jelly appears to offer very little resistance to the passage through it of the ionic micelle. This is a further confirmation of our theory of gel structure.

Curds also behave in the manner expected for even when the curd is firmly fixed in the tube so that a solution is being carried through it towards the cathode (the layer of extruded liquid being of course clearly visible on the cathode side) it is possible also to see the much smaller amount of clear layer formed by the ionic micelle advancing out of the curd towards the anode.

Stenolysis

Stenolysis is explained by our theory of surface layers binding one ion so that it cannot move and which therefore necessitates one ion carrying the whole of the current. At the end of the crack one ion is continuously being discharged into the solution and this must cause a considerable potential difference between the end of the crack and body of the solution. If the potential difference is greater than the decomposition potential of one of the ions present, it will be discharged electrically and thus deposited as metal or gas at an electrode. If the hypothesis is true, stenolysis should only be observed with ions of numerically low electrode potential and not with such ions as potassium, chlorine or iron.

Summary

1. Forty very complete experiments, involving 160 determinations of electrolytic migration have been carried out on the constituents in solutions of sodium oleate in the form of sol, gel and curd.

2. The chief results is to show that electrolytic migration, electrophoresis (cataphoresis) and electroösmosis (electrical endosmosis) are strictly identical.

3. A general formula

$$n_1 = \frac{c_1 m_1 f_1}{\mu}$$

expresses the actual movement relative to the solvent of each constituent of any electrically conducting system, whether homogeneous or heterogeneous, electrolytic, colloidal or involving electrical double layers or diaphragms. The movement of the solvent relative to any conducting constituent is $\frac{m_1 f_1}{\mu}$ kilos of solvent per faraday of current.

Velocity of electrophoresis and mobility are not identical although they have often been confused, for example in the study of proteins where the cataphoresis m_1f_1 has been interpreted as being the ionic mobility f_1. They are the same only when m_1 is equal to unity, that is when there is one electrical charge per chemical equivalent.

From this standpoint the only distinction between colloid and crystalloid is the number of chemical equivalents which are associated with one electrical charge.

4. In an electrical double layer such as that on the surface of a colloidal particle the particle itself seems to exhibit a conductivity per electrical charge almost comparable with that of an ion. Furthermore the corresponding ions of opposite sign in the solution forming the outer half of the layer maintain, unimpaired, the conductivity which they exhibit in the free state.

5. The relative movement of soap and water is found to be independent of whether the soap is moving as particles of jelly or as one mass of jelly or whether the water is forced to move through the soap jelly and the same value is obtained when the jelly is completely transformed into a fluid ordinary sol.

6. It is shown that electroösmosis can not be explained in terms of hydration or in terms of the frictional drag of a single ion.

7. The identity of these values for sol and gel affords further strong evidence for the conclusion that the colloidal particles in sol and gel are identical in nature and amount, save that in the jelly some of them are arranged possibly in filaments or other loose structure affording no additional resistance to the passage of the electrical current.

8. Whereas in dilute solution the migration of sodium oleate is that of an electrolyte, in the more concentrated solutions rather more sodium is moved towards the anode than towards the cathode. In a curd still more movement towards the anode is observed which may in some cases exceed five equivalents of oleate per one faraday of current.

9. The conducting constituents in all these cases are, sodium ion, small amount of simple oleate ion, highly conducting ionic micelle and the slightly charged undissociated soap. The undissociated soap moves one third times as fast as the ionic micelle and is therefore independent of the latter. Taking the values obtained for the constiuents of the soap sols, all the values for curds were in accordance with quantitative prediction. Likewise McBain and Bowden's data for potassium oleate are exactly confirmed. In the case of potassium laurate however the effective mobility of the undissociated soap is rather greater.

10. The hydration of soap in solution is found to be about ten mols of water for sodium oleate, thirteen for potassium oleate and not more than

seventeen for potassium laurate reckoned in each case per equivalent of total soap.

My cordial thanks are due to my colleague Prof. J. W. McBain for many valuable discussions and advice.

My thanks are due to the Colston Research Society of the University of Bristol, the Government Grant Committee of the Royal Society and the Research Fund of the Chemical Society for grants for materials and apparatus which rendered this investigation possible.

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THE CONCEPTION AND PROPERTIES OF THE ELECTRICAL DOUBLE LAYER AND ITS RELATION TO IONIC MIGRATION

BY JAMES W. McBAIN

It is becoming customary in biological and physical literature to express electro kinetic phenomena such as electroösmosis and the movement of colloidal particles in an electric field in terms of contact potential instead of recording the experimentally observed quantities. It is evidently not realised how large an element of speculation and of personal opinion is thereby introduced and that contact potential itself has never been satisfactorily measured, opinions varying even as to its order of magnitude.

All that has ever been observed is the relative movement of solid and liquid and the electromotive force which produces the movement or is produced by the movement. This statement embraces all four kinds of experiment; namely, electroösmosis, electrophoresis, streaming potential, and the electromotive force produced by falling powders. Contact potential, on the contrary, is not a matter of observation, but solely of inference. The formulation put forward by Miss Laing approaches this whole subject from a very different angle, and deals only with the experimentally observed quantities.

It has been found in all of the work in the Bristol Laboratory that the behaviour of ionic micelles as well as their accompanying ions is exactly like that of the ions of an ordinary electrolyte[1]. This involves a freer conception of the properties of the double layer which is extended in the preceding paper to all charged bodies and surfaces alike. Their properties are expressed in terms of mobility and conductivity and the actual charges concerned.

No one expresses the conductivity and migration of ordinary electrolytes in terms of the contact potential differences existing between their ions throughout the solution; such treatment being reserved for colloids and surfaces. Again in the calculation of contact potential the number of charges is left out of account, being eliminated with the thickness of the double layer. It is well therefore, briefly to review the basis of current conceptions of contact potential.

The fundamental paper upon this subject is that of Helmholtz[2], in which he synthesised the knowledge then available, and developed the conception and mathematical treatment of the double layer, which with slight modifications, is still in use. Previous to this he and a number of others had carried out experiments to ascertain the thickness of the double layer. Sir W. Thomson

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[1] McBain: Trans. Faraday Soc. 9, 99 (1913); Kolloid-Z. 12, 256 (1913); McBain and Salmon: J. Am Chem. Soc., 42, 426 (1920); Proc Roy. Soc. 97A, 44 (1920); cf. also the treatment by Pauli on parallel lines regarding colloidal gold as a free acid. Kolloid-Z. 34, 29 (1924).

[2] Wied. Ann. 7, 337 (1879).

had pointed out that two layers of opposite electrical charges such as the electrical double layer form, in effect, a condenser whose potential should be inversely proportional to their distance apart. He had come to the conclusion that charges on metals lay 0.3×10^{-8}cm. beneath their surface, and Helmholtz sought to find how far within a liquid the other charge of a double layer must lie. In his final experiments, he attached a Daniell cell to two pieces of platinum immersed in sulfuric acid carefully freed from gas, and from the amount of the momentary current which flowed without causing visible decomposition, he deduced that the charge within the liquid must lie one ten-millionth of a millimeter or 1 Å away from the platinum surface. This assumed that no decomposition whatsoever took place, that neither hydrogen nor oxygen is sorbed by, or dissolves in, or combines with, platinum to even an infinitesimal extent. But this is quite contrary to modern views; for example, the hydrogen and oxygen electrodes actually give a voltage about equal to that of the Daniell cell in place of the 1.23 volts expected, a fact which is currently attributed to the platinum becoming superficially oxidised. Helmholtz' conclusion is therefore invalidated, and a much greater thickness has to be ascribed to the double layer. Further, as Pellat[1] suggested, this value probably ought to be multiplied by the dielectric constant, which will again increase the thickness by at least eighty fold.[2] This latter point seems to have escaped the notice of most modern writers.[3]

A further consequence is to diminish in the same proportion the contact potential which Helmholtz and Lamb had deduced from the experiments of Wiedemann and Quincke; namely, five or ten volts as between a glass tube or a porous pot and an aqueous solution in contact with it. Such high values seem inadmissible in view of the fact that they greatly exceed those between the most active elements such as potassium and fluorine and aqueous solutions of their ions, although Cameron and Ottinger[4] published from Haber's laboratory as recently as 1909 experiments which they assumed to corroborate Helmholtz' value of five volts for the glass and water. It should be mentioned that, as is apparent from this historical sketch, not only is the contact potential diminished and the thickness of the double layer increased eighty fold but that the number of charges assumed is diminished in like proportion.

The recognition that the thickness of the double layer probably has to be increased by possibly 100 or 1000 fold, (owing to the faulty basis of Helmholtz' experimental evidence, as well as the introduction of the dielectric constant) deprives of its absurdity the assumption made by Helmholtz that the whole of the movement takes place within the double layer, and that the laws of viscous flow are exemplified within this film if liquid only half an atomic

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[1] See Perrin: J. Chim. phys., 2, 601 (1904).

[2] P. Walden recently obtained a large following for the idea that the dielectric constant in aqueous solutions of electrolytes might rise even to 14,000 which if so would increase the result 14,000 fold.

[3] See however Porter: Trans. Faraday Soc. 16, Appendix p. 137 (1921); who has hesitation in inserting the dielectric constant.

[4] Phil. Mag. (6) 18, 586 (1909).

diameter thick. Helmholtz was of the opinion that no slip occurred either between liquid and solid or between ions and the solution in which they are embedded, and that the whole of the movement is due to ordinary viscous flow within the part of the liquid within the double layer and although he formulated the effect of slip, he made no use of it. Lamb[1] was of the opposite opinion, but since Helmholtz had been able consistently to apply his equation, Lamb concluded that the facility of slip which he re-introduced must be of the same magnitude as the thickness of the double layer and so cancels out. If now the thickness has to be altered at least eighty fold by allowing for the dielectric constant, the argument requires revision. Smoluchowski[2] in 1914 could not decide on the basis of the evidence extant whether slip was a serious factor or not. Present opinion inclines to the view that slip does not occur. Coehn[3] for example, found that electro kinetic movement of acetone; water and propyl alcohol was proportional to the respective coefficients of viscosity. All who record their experiments in terms of contact potential make this assumption. A further argument in support of Helmholtz' opinion that slip will not occur is that the electric pull upon a monomolecular film of charges is only a few grams per square centimetre, whereas adhesives in shear on smooth surfaces such as glass withstand scores or even hundreds of kilograms per square centimetre.

We see that the thickness of the double layer within the liquid is greater than the mean distance between ions throughout the body of an ordinary solution (for 0.1N potassium chloride about $2\mu\mu = 20$Å). Now comes the fact that potassium chloride in solution conducts excellently and obeys Ohm's law and that the conductivity of a double layer such as that constituted by a particle of the ionic micelle in a soap solution together with its corresponding potassium ions is comparable charge for charge with that of potassium chloride. In both cases, in spite of the laws of electrostatic attraction, all the ions and charges are perfectly free to conduct, and no applied electromotive force is required to bring them into a conducting condition. These are experimental facts, although they have not been explained and in both cases the ions must be sufficiently far apart for this free movement to occur. The distance separating opposite charges will presumably be influenced by thermal vibration instead of being a fixed quantity, so that merely an effective mean value can be deduced. Hence, the true local values of the contact potential will likewise differ from the fictitious effective value inferred in accordance with the constantly changing positions of each of the mobile ions of the double layer.

It may now be pointed out that if the thickness of the double layer be taken as about 100 Å or $10\mu\mu$, a monomolecular layer of ions two Å apart would according to the accepted formulae for condensers[4], produce a contact

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[1] Report Brit. Assn. Adv. Sci., **1887** 495.

[2] Grätz: "Handbuch der Elektrizität", 2, 387.

[3] Z. Elektrochemie, **16**, 586 (1910).

[4] The voltage between plates $\epsilon = \frac{4\pi e\delta}{D}$ where e = elect. charge, δ = distance between plates and D = dielectric constant.

potential of 56 volts. Now the current tendency under the influence of Perrin[1] is to believe that the contact potential is about one thousandth of this, and if so, the conclusion would follow that the number of charges on the surface is only 0.1% of a monomolecular film, 99.9% being uncovered. If the applicability of the formulae be questioned, it must be remembered that they are assumed in each method of calculating contact potential hitherto, and it would seem preferable to record the experimental results in the form in which they are observed. Of course the dielectric constant need not be introduced, and the thickness of the double layer may once more be taken as 1 Å, a film so thin that both dielectric constant and viscosity lose their significance, but the difference of potential for a complete monomolecular film would still have the impossible value of 56 volts and there would still remain the interesting fact that the observed movements and electromotive forces produced depend directly upon the viscosity, and, as Coehn[2] has shown for twenty four liquids, upon the difference in dielectric constant of the solid and liquid.

There are still two directions in which modifications have recently been introduced into the conceptions underlying the formulae of Helmholtz, Lamb and Perrin. German writers are now convinced as a result of Freundlich's[3] experiments that the contact potential operative in electrokinetic phenomena ζ, is not the contact potential ϵ between the liquid and the solid as a whole, but that they may differ even in sign. The total contact potential ϵ is of course that which is measured in determinations of electrode potential, but it is considered that the greater part of this contact potential resides in layers of the solid and surface of the liquid that are incapable of movement, and that only the part of the contact potential ζ that corresponds to the remaining mobile ions of the double layer remaining within the liquid takes part in electroösmosis, etc. Further evidence to the same effect is deduced by the experiments of Coehn and Billiter, Borelius, and others.

Although Freundlich gives diagrammatic curves picturing how the absolute potential may change in passing from the body of the solid to the body of the liquid, he does not picture or discuss any mechanism in terms either of actual charges or ions, upon which of course all such potential changes must depend. He could for example (see below, Diagrams V to VII) have envisaged in the case we have just discussed, nearly all the charge on the liquid as consisting of a layer of ions adsorbed upon the outside of the solid surface while the mobile ions were at distances such as those previously discussed, and the layer of adsorbed ions need not have been all of one kind or sign.

Instead of this, Freundlich introduces another complication into the presumption of viscous flow of the double layer, opposite in nature to that introduced by Helmholtz' and Lamb's formulation of slip. He assumes a layer of immobile liquid of finite depth upon the face of the solid, embedding "part of the slope of potential," so that only the film of liquid between this and

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[1] Loc. cit.

[2] Ann. Physik. (4) 30, 777 (1909).

[3] Sitzungsber. preuss. Akad. Wiss. 20, 397 (1920); Coehn: Ann. Physik. (4) 48, 1005 (1915); Borelius; (4) 50, 447 (1916); Billiter: Z. Elektrochemie, 8, 638 (1902).

the mobile ions would be free to move with viscous flow. Probably few will follow his suggestion of an immobile layer of liquid if it is to be more than one molecule thick.

To sum up, when experimental results are expressed in terms of contact potential, and if these values are intended to possess more than an artificial significance, arbitrary assumptions are introduced concerning the nature of the flow, slip and immobilisation in excessively thin films of liquid, as to the thickness and position and distribution of the parts of the double layer and as to the influence of the dielectric constant with regard to all of which opinions vary most widely. It is sufficient also to refer to the calculations of Gouy[1], Wilson[2] and Mukherjee[3] with regard to the ionic equilibria involving the mobile ions of the double layer, the first emphasising the effects of concentration upon the thickness and distribution of the layer of mobile ions and the second suggesting the introduction of the Donnan equilibrium (principle of constant ionic product in the double layer and bulk of liquid).

It is helpful at this stage to turn to a few diagrams illustrating the customary conceptions which have been described. All the calculations have commenced with the consideration of the behavior of a capillary tube containing liquid with a complete double layer, such as is represented in longitudinal cross-section in Diagram I, although here the negative charges are placed in the outside of the solid surface like adsorbed ions rather than as free electrons just within the solid, as in Helmholtz' conception.

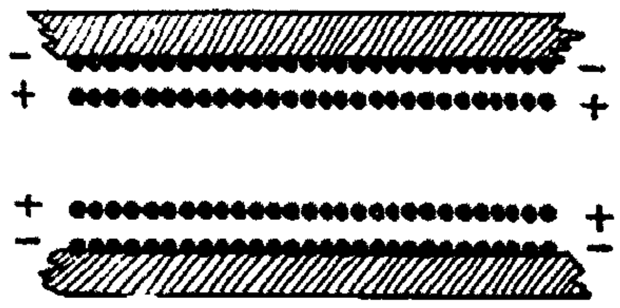

DIAGRAM I

Cross-section through a capillary tube showing the customary conception of a monomolecular double layer whose inner mobile ions form a complete sheath around the liquid in the body of the tube.

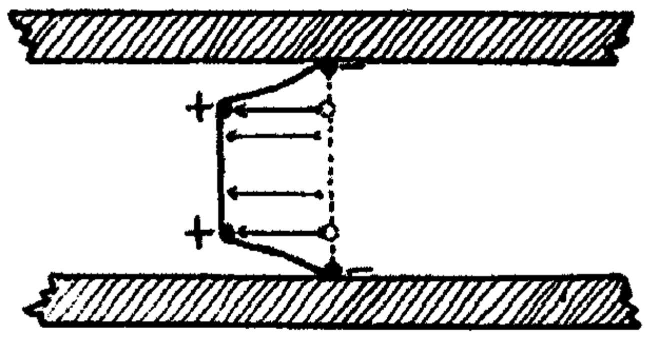

DIAGRAM II

The customary conception of electro-ösmosis (where no "slip" occurs) showing the movement and velocity of each part of a particular cross-section, the dotted line moving to the position shown by the full line a moment later.

Diagram II represents the flow produced by an electromotive force in such a tube, the dotted line representing any cross-section and the full line the position of the ions and fluid a few moments later. It is seen that the pull is exerted solely upon electrical charges and that all the liquid in the centre of the tube is pulled bodily along, in Lamb's phrase, "as it were by its skin". The diagram shows clearly the assumption made that there is no slip either at the walls or between the ions of the solution. The formula usually employed for

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[1] J. Phys. (4) 9, 457 (1910).

[2] "Chemistry of Leather Manufacture," 128 (1923).

[3] Trans. Faraday Soc. 16, 103; but see W. Harrison: 116 (1920-21).

the contact potential is that for a condenser of parallel plates and not that of concentric cylinders and the percentage error introduced is about one half of the percentage ratio of the thickness of the double layer to the radius of the tube[1]. Perrin's essential contribution was that if the curve showing change in flow for the different parts of the annular space enclosed by the double layer could be regarded as a straight line, then the force required to overcome viscosity would be inversely proportional to the thickness of the layer just like the number of charges in a condenser of varying thickness but constant potential. If this were so each definite movement would correspond to the same contact potential, no matter how the thickness or number of charges were varied. The error introduced by this assumption is equal to the ratio between the thickness of the double layer and the radius of the tube; it is therefore negligible for even a very fine capillary tube but becomes large for membranes whose pores are of colloidal dimensions and for colloidal particles. Perrin's other suggestion was that the formation of the double layer was due to differences in the size of ions, the smallest being able to get nearest to the walls, but according to his view the phenomena should have been independent of the nature of the wall.

Diagram III represents the stationary state when a constant hydrostatic pressure has been reached and a balance is obtained with the amount of solution flowing back according to Poiseuille's law.

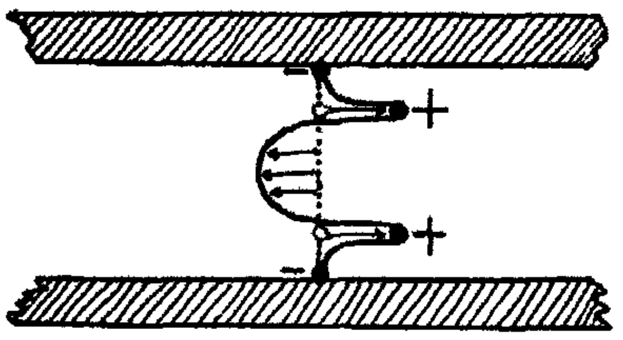

Diagram III
The Helmholtz conception of the stationary state where movement due to electroösmosis is just balanced by a counter hydrostatic pressure.

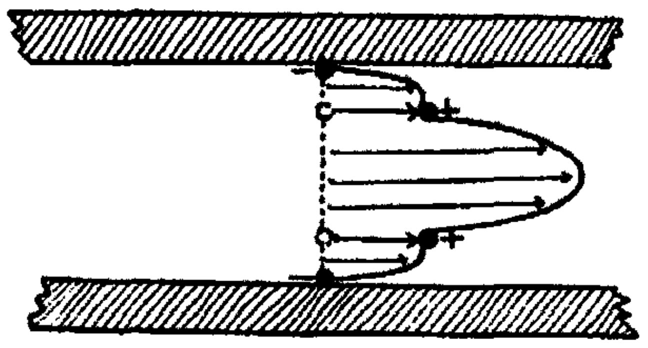

Diagram IV
The Helmholtz conception of the generation of electromotive force by solution streaming through a capillary tube.

Diagram IV illustrates the current potential or electromotive force produced by pressing the liquid through the capillary.

The fundamental assumption in all these previous calculations has been that the charges, or rather the mobile ions, form an effectively complete sheath, shutting off the body of the liquid in the tube from the annular space of the double layer. If this be so, the bulk of the liquid must move along with the mobile ions and in a migration experiment the mobile ions would not appear to have moved perceptibly relative to the solvent.

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[1] The expression for the velocity at any point in the annular space asuming viscous flow is of the form $v = \frac{k}{\eta} \frac{\ln R_1 - \ln r}{\ln R_1 - \ln R_2}$ where k is a constant, η the viscosity, R_1 the radius of the tube, R_2 the radius of the inner layer of charges and r the radius of any point within the annular double layer.

Now Miss Laing has pointed out that this does not represent the facts in sols, gels and curds of soap. Also we have seen that on the evidence given the layer of mobile ions instead of being a complete monomolecular sheath consists of scanty isolated ions. It is clear that this result can invalidate all the customary formulae, as is at once evident if we envisage the extreme case of one solitary mobile ion somewhere near the wall of a capillary tube. It must be some such reason that explains the demonstration that the mobile ions of the double layer move with their customary velocity through the solvent, which also moves, but more slowly.

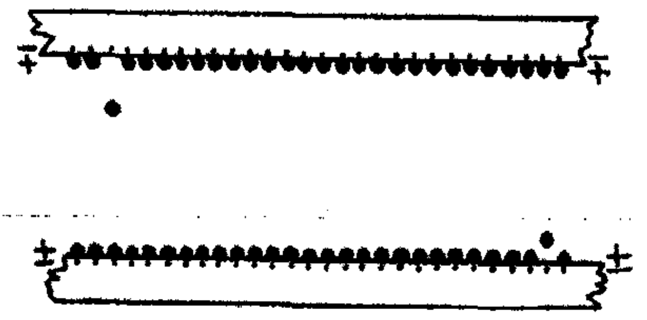

Diagram V

The conception of sparsely scattered mobile ions here advocated; nearly all the ions even of a complete monomolecular film are sessile and immovable: (N. B. There should be at the very most only two mobile ions in a length of tube one hundred and twenty times that shown.)

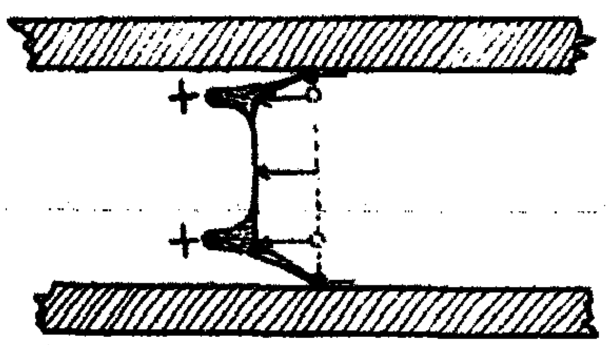

Diagram VI

The new conception of electroösmosis, two of the sparse mobile ions opposite each other, the bulk of the liquid being dragged at a slower speed past the walls and sessile charges.

Diagrams V to VII develop a new conception to take account of the sparcity of the mobile ions and the facts found by McBain and Salmon with the ionic micelle and by Miss Laing with gels and curds showing that both mobile ions and solid particles or wall move relative to the solvent. Further, the sessile immovable ions may be of opposite kinds, or few, or may form a practically complete adsorbed layer; a sessile ion may be balanced by a charge within the solid or by a mobile ion in the liquid (compare for example Diagrams V and VI).

Diagram V illustrates the view here suggested that only a very few of the ions in a double layer are mobile and that all the rest are sessile and immovable. Diagram V also shows very clearly the difference between the total or electrode potential ϵ (which would be about 0.5 volts if the dielectric constant is 81), and the much smaller and ambiguous electrokinetic potential ζ corresponding only to the sparsely scattered mobile ions. The diagram of course retains the assumption of no slip and of viscous flow.

Diagram VI shows electroösmosis where two of the isolated mobile ions are taken as being in the same cross-section of the tube, illustrating how the mean velocity of the liquid is much less than that of these ions.

Diagram VII is the counterpart of Diagram III but illustrates the stationary state for sparse mobile ions. After we had worked this out it came to our notice that Debye and Hückel[1] have made a similar assumption of visous drag of the ions in discussing the conduction of ordinary electrolytes and in supporting a value of 100% for their ionisation. For the sake of clearness we have not shown the whole liquid filled uniformly with ions which are often closer to each other than the mobile ions are to the wall; nor have we shown how the movements of the liquid is broken up by their conflicting movements which on the whole cancels out.

J. Stock[2] has published two papers which are interesting for both their theoretical and experimental treatment. He obtained one new and independent item of information by measuring the enhanced conductivity shown by probably impure nitrobenzene (commercial distilled from calcium chloride) when filled with powdered quartz. The results are only approximate on account of the numerous assumptions and corrections that it was necessary to introduce but they seem fairly definite. Experiments with other solvents were not very successful.

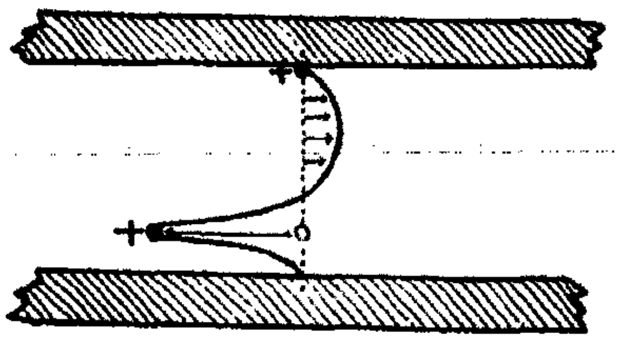

Diagram VII

The new conception of the stationary state in electroösmosis showing the movement caused by one of the sparse mobile ions.

Stock points out very clearly that if Helmholtz' theory is assumed as well as the current value for the contact potential, introducing the dielectric constant it is possible by combining these with Stock's own result to calculate the thickness of the double layer. Alternatively, if Lamb's theory is assumed it is impossible to determine either the thickness of the double layer or the contact potential but instead we deduce values for the facility of slip and the number of electrical charges involved.

Proceeding in this way and taking Coehn's value for the contact potential 0.053 which he confirmed by measurement of the electromotive force produced when quartz powder was dropped through a column of the nitrobenzene, and assuming Helmholtz' basis he deduced the thickness of the double layer 4.5 $\mu\mu$ or 45 Å from which he further deduces the mobile ions are 6.5 $\mu\mu$ apart. A further paper[3] in 1914 (which I have not succeeded in procuring) apparently contains similar measurements with ether and toluene.

Stock's results then, which are the only ones of their kind, seem to corroborate the view at which we have arrived in the present discussion that the mobile ions cover, at any given moment, only a small fraction of one per cent of the surface.

If the conception of the double layer with sparsely distributed mobile ions is true, two of the assumptions introduced by Helmholtz and employed

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[1] Physik. Z., 24, 305 (1923).

[2] Bull. (same as Anzeiger) Acad. Sci. Cracovie, 1912A, 635-656; 1913A, 131-143.

[3] Anz. Akad. Wiss. Krakau, 1914A, 95.

by every subsequent writer are invalidated. These are that in a given capillary tube the velocity of flow depends solely upon the value of the radius, $v = f(r)$; and secondly that along any line drawn parallel to the axis the velocity is strictly constant, $\frac{\delta v}{\delta x} = 0$.

It is evident that this fundamental subject affords a big field for theoretical and experimental elucidation. Fortunately it lends itself to both[1]. This opportunity may be taken to mention that the experimental study of conductivity and electroösmosis with surfaces of known dimensions of which a very preliminary account was given in the note of McBain and Darke in 1919[2] have been continued without intermission and that we hope to have a body of results suitable for publication within a reasonable period.

Summary[3]

Our present knowledge of the double layer between liquids and such materials as glass, membranes and colloidal particles is reviewed and the numerous and conflicting assumptions which have been put forward in calculating the "contact potential" are stated explicitly. It is emphasised that the contact potentials currently employed have a fictitious significance and it is therefore urged that experimental results be recorded in the form in which they are observed; namely, movement in an electric field or electromotive force set up by bodily movement.

A conception of the double layer with sparsely distributed mobile ions is developed which appears to harmonise the existing data including also those for absolute electrode potentials and for the behavior of sols, gels and curds of soap (cf. previous paper by Miss Laing). If this conception is a true interpretation of the existing data, the fundamental assumptions made in all previous mathematical treatment of this subject are invalid.

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[1] For example an explanation has to be found for the fact (originally pointed out by Müller "Chemie der Kolloide", p. 42 (1901); compare von Hevesy: Kolloid-Z. 21, 129 (1917) that ions, colloids and suspensions move at comparable velocities. Again it seems probable that the conception of migration of the constituents of the double layer may lead to a formulation of streaming potential which may admit of an experimental decision between this and other more orthodox views.

[2] Trans. Faraday Soc., 16, 150 (1920-21).

[3] Summarised accounts of this subject, each containing many references are to be found in: Freundlich: "Kapillarchemie" (1922) and partly rewritten 1923, (100 pages); Coehn: "Ergebnisse der exakten Naturwissenschaften" 1, 175 (1922), with 48 references; Burton: "Physical Properties of Colloidal Solutions" (1921), 33 references; Briggs: "Second Report on Colloid Chemistry", Brit. Assn. Adv. Sci. (1919), 61 references; also earlier summaries in Grätz, "Elektricität" (1914), and Wiedemann's "Elektricität" (1907).

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BLACK AND BLUE[1]

BY WILDER D. BANCROFT

In a recent paper,[2] I have pointed out that a possible reason for the apparent confusion between blue and black at the time of Homer was that blue may have been considered unconsciously as an intermediate stage between gray and black. I have just stumbled on what appears to be another case of confusion between blue and black in an article on indigo[3] published over a century ago.

"What Dioscorides calls *indicon* and Pliny and Vitruvius *indicum*, I am strongly inclined to believe to have been our indigo. It was a blue pigment brought from India, and used both in painting and in dyeing. When pounded, it gave a black powder; and when diluted in water it produced an agreeable mixture of blue and purple. It belonged to the costly dye-stuffs, and was often adulterated by the addition of earth. . . . Everything said by the ancients of *indicum* seems to agree perfectly with our indigo. The proper country of this production is India; that is to say, Gudcharot or Gutscherad, and Cambaye or Cambaya, from which it seems to have been brought to Europe since the earliest periods. It is found mentioned, from time to time, in every century; it is never spoken of as a new article, and it has always retained its old name; which seems to be a proof that it has been used and employed in commerce without interruption."

Beckmann states elsewhere in his article that "I have long made it a rule and prescribed it to others, in explaining any object mentioned by the ancients never to admit, without the strongest proofs, that the same article is denoted by different appellations. This, it is true, has been often done. By these means the small knowledge we possess of a thing that occurs under one name only may be increased. A wider field may thus be opened for conjecture, and more latitude may be given to the imagination; but at the same time one may fall into groundless explanations and hazard assertations, which, with whatever caution and learning proposed, will, on closer examination, be found either false or highly improbable. According to this rule, I have carefully endeavoured not to suffer myself to be so far misled by the respectability of my predecessors, as to consider the *Indicum* and *Indicum nigrum* of the ancients to be the same substance. On further research I find that the latter not only appears by the epithet to be different from indigo, but that it is China, or, as the Dutch call it, Indian ink. . . .

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[1] This paper is a necessary consequence of experiments supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Bancroft: J. Phys. Chem. 28, 131 (1924).

[3] Beckmann: "History of Inventions", 103 (1814).

"Pliny here enumerates all the materials which, in his time, were used for black ink. He, therefore, mentions two vitriolic substances, a slime or sediment (*salsugo*), and a yellow vitriolic earth (called also *misy*). Such minerals continued in use as long as men were unacquainted with the art of lixiviating the salt, and causing it to crystallize; or, in other words, as long as they had no vitriol-manufactories. He speaks also of lamp-black being made in huts built for the purpose, which are described by Vitruvius, and from which the smoke of burning pine-wood was conveyed into a close apartment. The article was certainly adulterated when soot, taken from the baths and other places where an open fire was maintained with wood of all kinds, was intermixed with it. It is very remarkable that black frcm burnt refuse of grapes, *noir de vigne,* which at present our artists, and particularly our copper-plate printers, consider as the most beautiful black, was made even at that period. Germany hitherto has obtained the greater part of this article from Mentz, through Franckfort, and on that account it is called Franckfort black. Some is made also at Kitsingen, Markbreit, and Munich. For this purpose the refuse of the grapes is charred in a close fire, and being then finely pounded is packed into casks. Pliny observes, that it was asserted that from this substance one could obtain a black which might be substituted for indigo. Another pigment was bone black, or burnt ivory, which is highly esteemed even at present. Besides these, continues he, there is obtained from India what is called *Indicum,* the preparation of which I have not yet been able to learn; but a similar pigment is made from the black scum of the dye pans, in places for dyeing black, and another kind is obtained from charred fir-wood finely pulverised. The cuttle-fish (sepia) likewise gives a black; but that however has nothing to do with the present question. He remarks in the last place, that every kind of black pigment is improved, or rather the preparation of it completed, by exposure to the sun; that is to say, after gum has been added to that intended for writing, and size to that destined for painting. But that which was made with vinegar was more durable, and could not be easily effaced by washing. All this is very true. Our ink acquires a superior quality when exposed to the light of the sun in flat vessels. That vinegar renders black colours faster, is well known to our calico-printers; and those who wish to have good ink must employ in making it the brightest vinegar of beer. It is equally true, that every black pigment mixed up with gum or size can be sooner and easier washed out again with water.

"A considerable part of what has hitherto been quoted from Pliny, may be found also in Vitruvius. The latter, in like manner, mentions huts for making lamp-black; he speaks also of ivory-black, and says expressly, that when it is properly made it not only forms a good colour and excellent ink, but approaches very near to *Indicum.*

"Now I might here ask, whether it is at all probable that the learned Pliny and the practical connoisseur of painting, the architect Vitruvius, could consider and describe our blue indigo as a pigment which, like lamp-black, could be employed as a black colour and as ink? Is it credible that Pliny, if he meant blue indigo in the before-mentioned passage, would have said that he was not able to learn the preparation of it, when he expressly describes it, as he believed it to be, in the course of a few lines further? Would Pliny and Vitruvius, had they been acquainted with black indigo only, remark immediately after, that, when costly indigo could not be obtained, earth saturated with woad, consequently a blue earth, might be used in its stead? Is not allusion here made to a blue pigment, as was before to a black one? Is it not therefore evident, that the name of *indicum* was given to a black and also to a blue pigment brought from India? And if this be the case, is it not highly probable that the black *indicum* was what we at present call India ink, which approaches so near to the finest ivory-black, and black of wine lees, that it is often counterfeited by these substances, a preparation of which is frequently sold as Indian ink to unwary purchasers? Indian ink is in general use in India, and has been in all probability since the earliest ages. In India all artificial productions are of very great antiquity; and therefore I will venture to say, that it is not probable that Indian ink is a new invention in India, although it may probably have been improved, and particularly by the Chinese.

"To confound the two substances, however, called indigo (*indicum*) at that period was not possible, as every painter and dealer in colours would know that there were two kinds, a blue and a black. It has, nevertheless, occurred to me, that in the works of the ancients obscurity may have sometimes been avoided by the addition of an epithet; and I once thought I had found in Pliny an instance of this foresight; that is, where he names all kinds of colours—*purpurissum*, *Indicum ceruleum*, *melinum*, *auripigmentum*, *cerussa*. I conceived that in this passage our indigo was distinguished from the black *indicum* by the epithet *ceruleum*. But my joy at this discovery was soon damped by Hardouin, who places between *Indicum* and *ceruleum* a comma, which is not to be found in many of the oldest and best editions. I cannot, therefore, get rid of this comma; for it is beyond all dispute that *ceruleum* was the common appellation of blue copper ochre, that is, mountain blue. I shall now proceed to examine whether my observation be true, that the Greeks frequently used the term black *indicum*, when they meant to denote the black, and not the blue.

"The term *nigrum Indicum* occurs in Arrian, Galen, Paulus, Aegineta, and perhaps in the works of other Greek physicians; and as the Latin writers were acquainted with an *Indicum* which dyed black, there is reason to conjecture that this was the *Indicum nigrum* of the Greeks, though I should rather be inclined to translate this appellation by the words Indian black, in the same manner as we may say Berlin blue, Roman red, Naples yellow, Brunswick green, Spanish brown, etc; or I should as readily translate it Indian ink. Arrian introduces it along with other Indian wares. I do not indeed find that he makes any mention of indigo properly so called; but a complete catalogue of merchandise is not to be expected from him. *Indicum*, however, occurs once more in this author; but in the passage where it is found it is only an epithet to another article. Speaking of cinnabar, he adds, that he means that kind called Indian, which is obtained from a tree in the same manner as gum. I am inclined to think that he alludes to dragon's blood, which on account of its colour was at that time called cinnabar.

"Some have conjectured that what in Arrian is named *laccos chromatinos* was our indigo, which indeed might be classed among the lakes, according to the present meaning of that word. Others, however, understand by it gum lac. But I am unacquainted with any proofs that gum lac was known at so early a period. I much doubt whether this meaning of the word lac be so old; and I must confess that the opinion of Salmasius appears to me highly probably, namely, that Arrian alluded to a kind of party-coloured garment. For, besides the grounds adduced by Salmasius, it deserves to be remarked, that in the passage in question different kinds of cloths, and no other articles, are mentioned. Besides, the epithet *chromatinos* is applied by the same writer, in the same sense to other kinds of clothing. It cannot, therefore, be said that Arrian mentions our gum lac, the origin of which word Salmasius endeavours to discover.

"In the works of Galen, which have not yet been sufficiently illustrated, I have found *Indicum nigrum* only four times. In a place there he speaks of diseases of the eyes, he extols it on account of its cleansing quality; and says it can be used for wounds, when there is no inflammation. In another place, it occurs in three prescriptions for eye-salves. I have however endeavoured, without success, to find in this excellent writer an explanation of what he calls *Indicum*; though he has explained almost all the different articles then used in the materia medica. It appears, therefore, that the Greeks gave the name of *Indicum* to our indigo, and also to Indian black or Indian ink.

"It, however, cannot be denied that, in opposition to this opinion, considerable doubts arise. Many who think that the black indigo (*nigrum Indicum*) of Pliny and Vitruvius was not ink, but our indigo, remark, that things of a dark blue or dark violet colour were by the Greeks and the Romans frequently named black; and, therefore, that the blue indigo might in this manner be called black. But the examples adduced as proofs are epithets, applied by the poets to dark-coloured flowers. Because nature produces no black flowers, the poets, who are fond of everything uncommon, extraordinary, and hyperbolic, call flowers black, when they are of so dark a tint as to approach nearly to black. Thus clear and deep water is called black. It is, however, hardly credible that painters and dyers, who must establish an accurate distinction between colours, should have spoken in so vague a manner. Salmasius suspects that *Nil* and *Nir*, the Arabic names of Indigo, have arisen from the Latin word *niger*.

"The objection, that Paulus Aegineta, the physician, in a passage where he refers to Dioscorides for the medical virtues of *Indicum*, applies to it the epithet black, seems to have more weight. It may be added also, that the virtues, in general, which Galen ascribes to the *Indicum nigrum*, appear to be similar to those ascribed by Dioscorides to *Indicum*; and the latter in one place, where he speaks of the healing of the wounds, uses only the expression *Indicum*, and not *Indicum nigrum*. It is particularly worthy of remark that Zosimus, the chemist, declares the hyacinth colour of the ancients, that of woad, and the *Indicum nigrum*, to be the same or similar. But to those who know on how slight grounds the ancient physicians ascribed medicinal qualities to many substances, it will not perhaps appear strange, that, in consequence of the same name, they should ascribe the same qualities to two different things. It is not improbable that in cases of external injury, for which the *Indicum nigrum* was recommended, indigo and Indian ink might produce as much or as little effect. I should consider of far greater importance the opinion of the chemist Zosimus; but unfortunately his writings have not yet been printed. The period in which he lived is still uncertain, and it is not known whether all the chemical manuscripts which bear that name were written by the same author.

"From what has been said, I think it may, at any rate, be inferred, that in the time of Vitruvius and Pliny indigo, as well as Indian ink, was procured from India, and that both were named *Indicum*. It is less certain that the Greeks called indigo *Indicum*, and Indian ink *Indian black*. Nay it appears that indigo, on account of the very dark blue colour which it exhibits both when dry and in the state of a saturated tincture, was often named Indian black."

It is interesting to note that the shading of blue into black is not unknown in the dye industry. Knecht, Rawson and Loewenthal[1] state that naphthol black B dyes wool from dark blue to deep black, while Ganswindt[2] points out that the black acid colors do not give a pure black on silk but dye a very dark blue even when used in fairly high concentrations. Even in this case there is some question as to the actual color for Matthews[3] says that "the acid dyes are principally used on silk for the production of fancy colors; the black acid dyes, though largely used on wool, have but little use on silk as it is not possible to produce as satisfactory a black with them as with logwood. The black acid dyes do not seem to properly fill the fiber so as to make it opaque to light, in consequence of which the color exhibits a slaty appearance, while with logwood (by reason of the relatively large amount of pigment mordant employed) the fiber is rendered opaque and the color produced is a full rich black."

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[1] "A Manual of Dyeing", 558 (1910).

[2] "Theorie und Praxis der modernen Färberei", II 44 (1903).

SOME PHYSICAL-CHEMICAL PROPERTIES OF MIXTURES OF ETHYL AND N-PROPYL ALCOHOLS

BY GEORGE S. PARKS AND JULIUS RAE SCHWENCK

In recent years the concept of an ideal or "perfect solution" has become prevalent. Such a solution is one whose properties may be expressed in terms of the fractions of the components and the original properties of the pure substances by means of simple laws. Thus, in an ideal mixture of two liquids, the components should be miscible with one another in all proportions; the partial pressure of each component should follow Raoult's law[1]; and the volume and heat content of the resulting mixture at any temperature should be the sum of the volumes and the heat contents of the pure substances used —in other words, there should be no volume change or heat effect on formation of the mixture.

From *a priori* considerations it would seem that mixtures of ethyl alcohol and normal propyl alcohol should closely approximate to these requirements. The two components involved are neighboring members of a homologous series and due to this close chemical relationship are very similar in certain important physical properties, as the following table will indicate.

TABLE I

	Dielectric Constant[2]	Capillary Constant[2]	Association Factor[3]	Internal Pressure[4]	
				Winther	Traube
C_2H_5OH	25.8	1.083	2.74	2030	2160
C_3H_7OH	22.2	1.234	2.25	1900	1800

The relatively small differences in the dielectric constants and the comparable values for the capillary constants and association factors indicate that the two liquids are about equally polar. Also the internal pressures, calculated by Winther from optical properties and by Traube from surface tension and van der Waal's "a" and "b", are of the same order of magnitude. All these factors—chemical similarity, equal polarity, and comparable internal pressures —would lead us to suspect that this pair of liquids might form solutions which would be almost "perfect".

Up to the present time, however, only very scanty experimental evidence on the subject has been available. Bose[5] has determined the heat effect at 21°C for the formation of solutions containing 49.6% and 32.9% (by weight) of ethyl alcohol and found the values $-.125$ cal. and $-.140$ cal. respectively

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[1] G. N. Lewis: J. Am. Chem. Soc. **30**, 668 (1908).

[2] Abegg and Seitz: Z. physik. Chem. **29**, 242 (1899).

[3] Ramsay and Shields: Z. physik. Chem. **12**, 468 (1893).

[4] Hildebrand: J. Am. Chem. Soc. **38**, 1459 (1916).

[5] Bose: Göttingen Ges. Nachr. **1906**, 333.

for the heat of mixing per gram of solution. These small values were almost within the limits of his experimental error and in a second publication[1] he briefly dismisses the subject with the statement that the heat of mixing of the alcohols studied (i.e. methyl, ethyl, and n-propyl) was approximately zero.

Recent specific heat determinations[2] on ethyl alcohol, n-propyl alcohol, and an equi-molal mixture of the two indicated that, within the limits of experimental error, the pure substances retain their original heat capacities after formation of the equi-molal mixture—a property of perfect solutions. These two researches seem to provide the only information applicable to this interesting binary system and it was for this reason that the work described in the present paper was undertaken. While the results obtained are of only moderate accuracy, it is felt that the absence of any similar data renders their publication desirable.

Experimental

Purification of Substances. A good commercial grade of 95% ethyl alcohol was dehydrated by a preliminary distillation over lime in the ordinary manner, followed by a second distillation over a small quantity of calcium metal. The resulting product was carefully fractionated and the middle portion, about 60% of the total, was selected for use in the following experiments: $D^{25^\circ}_{4^\circ}$ 0.78540, which corresponds to 99.9% ethyl alcohol according to the U. S. Bureau of Standards tables.[3]

The normal propyl alcohol was obtained by a similar process from a sample of "refined" commercial product, initial boiling point 96°-98° C. After distillation with lime, with metallic calcium, and fractionation, a liter of the original material yielded 575 cc with a density of 0.8004, corresponding to about 993/4% alcohol on the basis of Brunel's[4] value of 0.7998 25°/4° for 100% and the variation per 1% of water of 0.0026 obtained from Landolt-Bornstein-Roth[5].

Determination of heat of mixing. The alcohols thus prepared were used in making a series of seven mixtures, which varied systematically in steps of approximately 12.5% of each component. Thus the first mixture contained by weight 87.50% of ethyl alcohol and 12.50% of the n-propyl alcohol; the second mixture, 74.93% ethyl and 25.07% propyl, etc. About 100 cc of each mixture was made up.

In the course of the preparation of these solutions the heat of mixing was determined at 25°C. This was accomplished by placing the proper weight of the component which was to be present in greater quantity in any particular case in a half-pint Dewar jar, equipped with a calibrated Beckmann thermometer, a stirrer of the propeller type and a tightly-fitting cork cover to exclude

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[1] Bose: Z. physik. Chem., **58**, 611 (1907).

[2] Gibson, Parks and Latimer: J. Am. Chem. Soc. **42**, 1542 (1920).

[3] U. S. Bureau of Standards. Scientific Paper, No. 197 (1913).

[4] Brunel, Crenshaw and Tobin: J. Am. Chem. Soc. **43**, 574 (1921).

[5] Landolt-Börnstein-Roth: Tabellen, p. 307 (1912).

moisture. The required weight of the other component was then placed in a half-pint Dewar bottle also equipped with a calibrated Beckmann thermometer, the zero of which was checked daily with that of the Beckmann in the jar.

When the two liquids had reached approximately the same temperature, that in the bottle was quickly poured via a thistle-tube lead into the Dewar jar which served as the calorimeter, the mixture was stirred for two minutes at a rate of 80 R.P.M. and then allowed to stand for a similar period after which the final temperature was taken. By at once repeating the stirring and waiting interval and again reading the Beckmann, the temperature correction due to stirring, heat exchanges with the surroundings, etc. was obtained. The corrected temperature change was then used for calculating the heat effect in producing one gram of the solution under consideration. This calculation was made in the usual way, using 6.0 cal. as the heat capacity of the calorimeter and .582 and .570 cal. as the specific heats at 25°C. of pure ethyl and pure propyl alcohol respectively. The heat capacity of each mixture was taken as the sum of the heat capacities of the pure components, a procedure which the work of Gibson, Parks and Latimer had shown to be justified. The results are given in Table II.

TABLE II

Heat of Formation of the Mixtures at 25°

Liquid	% C_2H_5OH by weight	Mol. fraction of C_2H_5OH	Heat of mixing in calories per gram of mixture	Heat of mixing in calories per mol of mixture
1	100.00	1.000	——	——
2	87.50	.902	−.036	−1.7
3	74.93	.796	−.058	−2.8
4	62.40	.684	−.079	−4.0
5	50.02	.566	−.092	−4.8
6	37.49	.439	−.089	−4.8
7	25.00	.303	−.078	−4.3
8	12.54	.158	−.054	−3.1
9	0.00	.000	——	——

The numbers given in the first column to the various liquids are for convenience in reference in subsequent pages of this paper. Thus, when we mention "liquid No. 4" for instance, we shall be referring to the solution containing 62.40% (by weight) of ethyl alcohol. The process of forming the various solutions took place with the absorption of heat and the values in calories for the production of 1 gm. and 1 mol of mixture are given in columns 4 and 5 respectively. It will be noticed that our value for liquid No. 5 is −.092 cal. per gram of mixture, while Bose obtained −.125 for an almost identical concentration. Certainly it is evident that the heat effect is very small throughout the entire range of concentrations—an indication that we are dealing with solutions that are not far from perfect.

Densities and Refractive Indices. The densities of the liquids thus made up were next determined in the usual manner, using a specific gravity bottle of about 50 cc capacity. Corrections were made for the buoyancy of the air, and the final values appear in the second column of Table III; they are probably accurate to the extent of ± .0001 gm. per cc. For purposes of comparison determinations were also run on samples of the pure alcohols after they had been put thru the stirring process, etc. in the Dewar jar described in the previous section. This was done because it seemed inevitable that the samples would absorb traces of moisture during such a calorimetric procedure and we desired to have all our liquids in as comparable a condition as possible.

The refractive indices for sodium light were then determined with a Zeiss-Pulfrich refractometer, the method of Moore[1] for temperature measurement being employed. This ingenious method obviated all necessity of using thermostatic devices and permitted us to express our results for the standard temperature of 25°C.

Table III

(Temperature, 25°C)

Liquid	Density		Refractive Index	
	Observed	Calculated	Observed	Calculated
1	0.7863	———	1.3590	———
2	0.7886	0.7882	1.3619	1.3620
3	0.7904	0.7901	1.3649	1.3651
4	0.7923	0.7921	1.3681	1.3681
5	0.7942	0.7940	1.3712	1.3712
6	0.7961	0.7959	1.3742	1.3742
7	0.7979	0.7979	1.3772	1.3772
8	0.8000	0.7998	1.3803	1.3803
9	0.8018	———	1.3833	———

In the formation of a perfect solution the resulting volume should be equal to the sum of the original volumes of the components involved, or in terms of densities the relationship is

$$\frac{100}{D} = \frac{1}{d_1}P_1 + \frac{1}{d_2}P_2$$

where d_1 and d_2 are the densities of the components in the pure state, P_1 and P_2 are their corresponding weight percentages in the resulting solution and D is the density of the solution. Using this equation, we obtained the calculated densities appearing in column 3 of the preceding table. These values average less than .03% lower than the observed densities of column 2, and this fact indicates that the original assumption of "idealness" for these alcohol mixtures is very close to the truth.

The refractive indices of the pure alcohols differ by only .0243 and the densities by .0155; hence it was not considered worth while to apply the

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[1] Moore: J. Phys. Chem. 25, 281 (1921).

relationship of Lorentz and Lorenz[1] to this set of liquids. Instead the refractive indices appearing in the fifth column were calculated by the simple equation

$$100\, n = P_1 n_1 + P_2 n_2$$

where n_1 and n_2 are the indices of refraction for the pure liquids, P_1 and P_2 being their respective weight percentages in any given solution. Comparison of these calculated values with the observed shows that for this system the procedure is fully justified. The straight line relationship between the index of refraction and the weight composition of the solution, coupled with the fact that only an extremely small quantity of liquid is required for the measurement, renders this an excellent analytical method for determining the composition of an unknown mixture of the alcohols. The instrument used could be easily read with an accuracy of ± 1 minute, while the two pure alcohols differed by 4°22'; hence analysis to better than .4% is feasible.

Viscosities. Next we ran the viscosities for all the liquids, using an Ostwald viscosimeter in a 25° C. thermostat, regulated to .005°. The value of 0.00893 dynes per sq. cm., as obtained by Hosking[2] was assumed for the water which was used in standardizing this instrument. The time, measured by a stop-watch, averaged around 100 seconds and thus limited the accuracy of these results to ± .00003 dynes per sq. cm.

TABLE IV

Viscosities at 25° C (in dynes per sq. cm.)

Liquid	Observed values	Calculated (Kendall's equation)	Calculated (Logarithmic equation)
1	.01090	———	———
2	.01169	.01157	.01151
3	.01233	.01231	.01221
4	.01319	.01314	.01299
5	.01408	.01404	.01387
6	.01522	.01506	.01488
7	.01640	.01621	.01604
8	.01759	.01750	.01738
9	.01897	———	———

The viscosities as determined range from .01090 for ethyl alcohol to .01897 for the propyl and, while there seems to be no really satisfactory equation for the viscosities of mixtures, the system under consideration provides a means of testing out two of the more promising relationships. Accordingly, in column 3 of Table IV appear the values calculated by use of the cube-root equation suggested by Kendall[3]:

$$\eta^{1/3} = x_1\eta_1^{1/3} + x_2\eta_2^{1/3}$$

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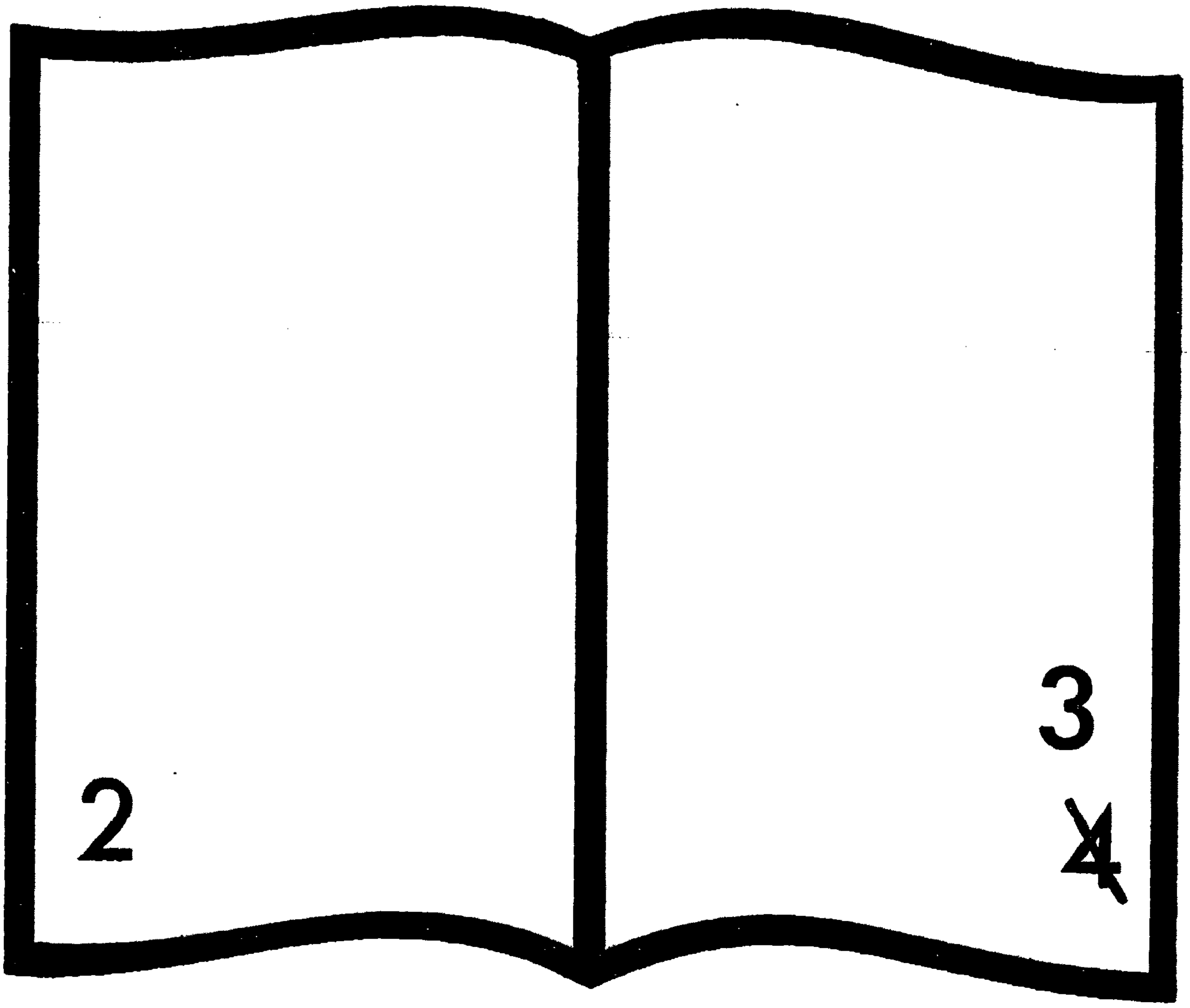
[1] Nernst: Theoretical Chemistry, p. 114 (1923).

[2] Hosking: Proc. Roy. Soc. N. S. Wales, 43, 37 (1909).

[3] Kendall: J. Am. Chem. Soc. 42, 1776 (1920).


2
3
~~4~~

where η_1 and η_2 are the viscosities of the pure components and X_1 and X_2 are their respective mol fractions. The logarithmic relation,

$$\log \eta = x_1 \log \eta_1 + x_2 \log \eta_2$$

was also tried and the results obtained appear in the last column. It is evident from the data that Kendall's equation is better throughout the entire range of mixtures, being on the average about .65% low while the latter is 1.6% low.

Boiling Point and Distillate Composition. The boiling points of the various liquids were determined to the nearest 0.1°. This was accomplished by placing a 25 cc sample in a small distilling flask fitted with a condenser. The liquid was gradually brought to boiling and, at the time of delivery of the first drop of distillate, the temperature was read by a calibrated mercury thermometer, graduated to 0.1°C. When about 1 cc of distillate had passed over, the process was stopped and the composition of this distillate determined by measurement of its refractive index. The experimental results appear in columns 2, 3 and 4 of the following table.

TABLE V

Boiling points and Distillate Composition.
Barometer, 761 mm

Liquid	Boiling Point	C_2H_5OH in distillate % by weight	Mol fraction	Partial Pressure of C_2H_5OH Observed	Calculated
1	78.4°C	100.0	1.000	761	762
2	79.8	93.0	.946	720	726
3	81.4	86.0	.886	674	678
4	83.1	77.4	.813	619	622
5	85.0	68.8	.738	562	555
6	87.1	58.3	.641	488	467
7	89.3	43.5	.499	380	351
8	92.7	22.3	.269	205	207
9	97.2	0.0	.000	0	0

In the fifth column we have the partial pressures of ethyl alcohol in the various solutions computed from the observed total pressure (761 mm) and the mol fraction of ethyl alcohol found in the distillate; while in the next column are inserted for purposes of comparison the values calculated by the use of Raoult's law. For obtaining these latter results it was necessary to have the actual vapor pressure of pure ethyl alcohol at each of the observed temperatures. This was found by plotting on large coordinate paper the pressures and temperatures as given by the Landolt-Börnstein-Roth Tabellen (page 387) and then reading off from such a graph the pressure corresponding to the observed boiling point of each solution.

Total Pressures and Partial Pressures at 25° C. The composition of the vapor phase in equilibrium with the solutions at 25°C. was determined. This was accomplished by passing air (freed from water and carbon dioxide) through a pair of bubblers, each containing about 20 cc of the mixture under consideration. The bubblers were immersed in water baths kept within 1° of 25°C; closer temperature control is not necessary as the percentage composition of the vapor phase changes very little between 25° and the boiling point. The air thus saturated with the vapor of a mixture was then passed thru a condensing tube immersed in liquid air; the alcohol separated out as a solid glass on the walls of this tube and, when about 1 cc of distillate had been collected, was analyzed by the refractometer method previously described. The results appear in Table VI.

TABLE VI

Ethyl Alcohol in the Vapor of the Liquids at 25° C.

Liquid	% by weignt	Mol fraction of C_2H_5OH
1	100.0	1.000
2	92.6	.942
3	87.5	.902
4	79.3	.833
5	71.5	.767
6	60.3	.662
7	45.5	.521
8	27.0	.326
9	0.0	.000

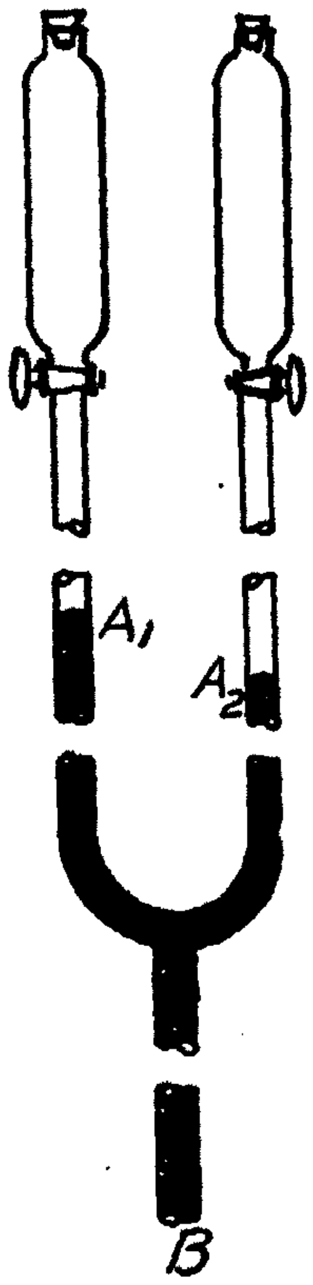


FIG. I

Our intention had been to determine also the total pressure of each liquid in the series but this measurement was postponed to the very last. Press of other work delayed us for about a year and then, as it seemed possible that the original mixtures might have undergone some change or contamination during the interval, a new set of four solutions was made up specially for this phase of the work from the pure alcohols[1].

The difference between the total pressure of the ethyl alcohol and each other liquid in this new series was determined by a differential method, utilizing a glass apparatus similar in form to the accompanying diagram. Ethyl alcohol, as the reference substance, was placed in the side-arm A_1 which was closed at the top by a tested stopcock S_1 while the other liquid was placed in the arm A_2, being poured in via a similar stopcock S_2. The lower end of the apparatus at C was connected by pressure tubing with a mercury reservoir which could be raised or lowered as desired and which was carefully manipulated so that at all times the level of mercury was well above

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[1] For the preparation of these new solutions and the subsequent measurement of their respective vapor pressures, we are indebted to Mr. O. S. Lovekin of this laboratory.

the fork B and thus the two liquids were kept entirely separate. The procedure was to introduce by the two stopcocks 5 cc. samples into each arm of the apparatus, then to lower the mercury reservoir until a small vapor phase was produced and wait a few minutes. During this time much of the air dissolved in the liquids was evolved and could be forced out of the apparatus by raising the mercury level and simultaneously opening the two stopcocks to permit of its escape. By repeating this operation two or three times all the air originally in the samples could easily be removed. Then the mercury reservoir was so adjusted as to permit the existence of a small vapor phase and the difference in mercury levels in the two tubes was measured by a cathetometer at quarter-hour intervals, the temperature registered by a thermometer placed between the two arms being noted at the time of each reading. Corrections, when necessary, were made for any differences in the columns of alcohol liquid in the two arms. These measurements were all made in a small room in which the temperature could be kept very close to 25° C and any departure from this standard point (seldom more than a few tenths of a degree) could be easily corrected for by a rough determination of the rate of change of this pressure difference with temperature in each particular case.

Regnault's value of 59.0 mm. as corrected by Bunsen[1] was taken as the vapor pressure of the ethyl alcohol and, by means of the differences measured in the manner just described, the vapor pressure of each of the five remaining liquids was computed; the results appear in the following table, column 4.

TABLE VII

Data for New Set of Mixtures

Liquid	Mol fraction of C_2H_5OH in liquid	Mol fraction of C_2H_5OH in vapor phase	Vapor pressure of liquids Experimental	"Ideal"
1	1.000	1.000	59.0 (assumed)	——
A	.836	.924	53.0 mm	53.1 mm
B	.656	.823	47.5 "	46.7 "
C	.459	.678	40.4 "	39.7 "
D	.241	.440	32.3	31.8
9	.000	.000	23.2	——

The values (column 3) for the composition of the vapors in equilibrium with these new solutions were not determined directly but were obtained graphically from a smooth curve representing the data of Table VI. In this sense they are really experimental and, when multiplied by the corresponding total pressures for the various solutions, give us the observed partial pressures of ethyl alcohol appearing in column 2 of Table VIII. The observed partial

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[1] Landolt-Börnstein-Roth: Taballen, p. 386 (1912).

pressures of normal propyl alcohol were obtained in similar fashion. The "ideal" pressures in all cases were derived on the assumption of Raoult's law:

$$p_A = N_A P_A$$

where p_A and N_A are respectively the partial pressure and the mol fraction of component A in a given solution and P_A is its vapor pressure in the pure state.

TABLE VIII

Partial Pressures of the Components at 25°C.

Liquid	Partial pressure of C_2H_5OH Observed	Partial pressure of C_2H_5OH Ideal	Partial pressure of C_3H_7OH Observed	Partial pressure of C_3H_7OH Ideal
1	59.0 mm	———	0.0 mm	———
A	49.0 "	49.3 mm	4.0 "	3.8 mm
B	39.1 "	38.7 "	8.4 "	8.0 "
C	27.4 "	27.1 "	13.0 "	12.6 "
D	14.3 "	14.2 "	18.0 "	17.6 "
9	0.0 "	———	23.2 "	———

It will be noticed that on the whole the values derived from our experimental data are somewhat higher than those called for on the assumption that we are here dealing with ideal or perfect solutions. This deviation, however, is the usual one when heat is absorbed on the formation of a mixture from the pure components.

The Entropy of an Equi-Molal Mixture. In this connection it is interesting to check up on an assumption made by Gibson, Parks and Latimer. They needed the entropy change for the process

$$1/2 \text{ mol EtOH} + 1/2 \text{ mol PrOH} = 1 \text{ mol of mixture}$$

and, in the absence of the proper data, obtained the value 1.37 cal. per degree by assuming that the two alcohols form a perfect solution.

We now are in a position to calculate the entropy change by means of the thermodynamic equation

$$\Delta F = \Delta H - T\Delta S \quad .$$

By plotting our figures for the partial pressures of the two alcohols against the corresponding mol fractions, drawing smooth curves and reading from these the partial pressures of each in an equi-molal mixture, we obtain 29.8 mm and 12.2 mm as the respective values for ethyl and n-propyl alcohols. From these ΔF, the free energy change at 25°C for the above process, can be found:

$$\Delta F_{25°C} = 298R[\tfrac{1}{2}\ln\frac{29.8}{59.0} + \tfrac{1}{2}\ln\frac{12.2}{23.2}] = -393 \text{ cal.}$$

Then from our data on the heat of mixing, we obtain 5 cal. as the increase in heat content for the production of the mol of mixture. Hence, $\Delta S_{25°C} = \frac{393+5}{298} = 1.34$ cal. per degree, a result almost identical with that calculated on the assumption of an ideal solution.

Summary

Reviewing the results of the various measurements, we find that

(1) A very small heat absorption (in no case more than 5 calories per mol of resulting mixture) takes place on formation of the several solutions.

(2) An extremely small volume shrinkage—on the average only .025% —accompanies the process.

(3) The refractive indices of the various liquids are practically a straight line function of their weight compositions.

(4) The observed viscosities for the various solutions exhibit on the average a positive deviation of 2/3% from Kendall's "cube root" equation.

(5) The partial pressures of each component as calculated from the experimental data at 25° C are in general slightly higher than those called for on the basis of Raoult's law.

Judging these facts as a whole, we may conclude that the system under consideration is almost "perfect".

Department of Chemistry
Stanford University, California
March 10, 1924.

THE OPTICAL INACTIVITY OF THE ACTIVE SUGARS IN THE ADSORBED STATE:—A CONTRIBUTION TO THE CHEMICAL THEORY OF ADSORPTION. I

BY SHANTI SWARUP BHATNAGAR AND DASHARATH LAL SHRIVASTAVA

There are at present three well-known theories regarding the mechanism of protective action of colloids:

(1) That the protecting agent concentrates at the interface of the colloid particles and the dispersion medium according to Gibbs-Thomson law, and forms a mechanical envelope round them, thus protecting them from coalescence. Familiar examples of this kind of action are emulsions prepared from oil and water with the aid of soaps as emulsifying agents.

(2). That the protecting agent on adsorption by the colloidal particles increases the density of the charge on them and thus confers greater stability. Protection by similarly charged colloids fall in this category.

(3). That on account of the chemical affinity the protecting agent and the colloid particles join hands as it were and acquire greater stability. Zsigmondy[1] has given a very beautiful example of this in the case of gelatin adsorbed by gold foil.

The fact that sugars have protective action is well-known. They are generally used as peptising agents[2] and it is therefore interesting to know as to which of these theories can explain the mechanism of the protective action of the sugars satisfactorily.

'A priori' it is clear that the application of the second theory is not probable as sugars in aqueous solutions do not exist as charged particles, and thus the choice would fall between the first and the third theories. If the protection is a purely physical phenomenon then the optical rotation of the solution mixed with sugar would be as follows:—

Let the original rotation of the sugar solution be β, and further let 'a' c.c. of this be diluted with 'na' c.c. of a collodial solution where n is a positive integer. Then on Beer's law,

$$\text{the new rotation } \beta' = \frac{\beta}{n+1} - x \qquad (1)$$

where x denotes the rotation corresponding to the decrease in the effective length of the polarimetric tube, due to the presence of suspended particles; x is a factor which is determined experimentally as described later on.

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[1] "The Chemistry of Colloids, 112 (1917).

[2] Bancroft: Second Colloid Chem. Rep. Brit. Assn. 1919, 2.

If however, chemical forces as postulated by Zsigmondy and Langmuir are operating, the optical rotation of the system may undergo anomalous change.

It was with a view to obtain information regarding this point that the present investigation was undertaken. Incidentally it has thrown much interesting light on the mechanism of adsorption as would be apparent from the discussion of the results.

Experimental

The colloidal solutions used were those of arsenic and antimony hydrosulphides. The former sol was prepared by dissolving Kahlbaum's pure arsenious oxide in distilled water and then by passing hydrogen sulphide gas for sometime. The excess of the gas was removed by bubbling in a rapid current of hydrogen gas through the solution. Similarly antimony hydrosulphide sol was prepared by dissolving Merck's potassium antimony tartrate in distilled water and by passing sulphuretted hydrogen and getting rid of the excess as described above. The former sol was marked A/1 and the latter B/1.

The quantity of the equivalent amounts of As_2O_3 and $Sb_2 O_3$ in A/1 and B/1 respectively were determined volumetrically by the Kessler's method[1]

Four samples marked A/1, A/2, A/3, A/4 were prepared from A/1 by diluting it with water; the ratio of sol to water being respectively 1:0, 1:1, 1:2, 1:3. Similarly different samples B/1, B/2, B/3, B/4 were prepared from B/1 sol. All these were preserved in well-stoppered bottles.

Optically active sugars used were Merck's sucrose, glucose, and galactose. Solutions of these were prepared by dissolving them in distilled water. The optical rotations were measured by the Tripartite field, International Sugar Scale Polarimeter manufactured by Adam Hilger Ltd. The tubes used were the water-jacketed 50 mm. and 220 mm. ones. The monochromatic light used was the arc lamp with a potassium bichromate filter, the sodium light being found too feeble for these experiments.

First of all, the specific optical rotations of the three sugars for the particular light used were determined. After this a solution of sugar to be experimented upon was prepared and its rotation measured. Then a sample of the colloidal solution was taken and three dilutions of the sugar solution were made in which sugar and colloidal solutions were in the ratio of 1:1, 1:2, and 1:3. In order that the volumes of the two taken out for the dilution may be the same, the same pipette was used for measuring the volume of the liquids, special care being taken in washing and rinsing the pipette when taking in any liquid. Such dilutions as above were made in the case of all the samples.

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[1] Pogg. Ann. **118**, 17 (1863).

But before doing regular experiments, attempts were made to determine the factor x in equation (1). Two series of experiments were performed.

(1) In the water-jacketed polarimeter tube there is an opening through the water jacket, in the middle, so that any liquid to be examined can be poured into the tube without opening it at any one of the ends. Advantage was taken of this to put in small crystals of aluminium chloride into the tube containing the mixture of the solution and sugar. The addition of $AlCl_3$ resulted in the settling down of the particles. The reading in the polarimeter was again taken, and some of the results are given below in Table I.

(2) The mixture of the sol and sugar solution was coagulated outside and the rotation due to the supernatant liquid was examined. The results of these also are given below in Table I, column 3.

TABLE I

All the values of rotation given in this table are positive.

1 Rotation of the mixture of the sol and sugar solution.	2 Rotation after the coagulation of the solution in the tube.	3 Rotation of the supernatant liquid obtained by coagulating the sol particles outside the tube.
0.84	0.84	0.84
0.41	0.41	0.41
0.58	0.58	0.58
1.66	1.66	1.66
1.83	1.83	1.83
2.51	2.51	2.51

From the above table it is clear that the effect of the presence of the particles on rotation are, if any, undetectable i.e. the factor x is negligible.

Therefore the equation becomes

$$\beta' = \frac{\beta}{n+1} \qquad (2).$$

After this the rotations of the various mixtures of sols and sugars prepared as described above, were examined and the results are entered in Tables II-VIII.

TABLE II

Optically active substance used: Sucrose.

Specific rotation of sucrose taken = +67.5

50 mm. tube used.

Original rotation (β) = +3.41

Quantity of sucrose per 100 c.c. of the solution = 10.104 gm.

Colloidal substance used: Arsenious hydrosulphide sol containing arsenic equivalent to 1.188 gms. of As_2O_3 per litre.

Equivalent quantity As_2O_3 per litre.	Ratio of the original sucrose solution to the sol.	Rotation expected on equation (II). $\left(\frac{\beta}{n+1}\right)$	Actual rotation observed. (β')	Quantity of sucrose present per 100 c.c. of the mixed solution examined	Quantity of sucrose adsorbed per 100 c.c. of the mixed solution examined.	Quantity adsorbed per 100 c. c. of the sol.
A/1	1:1	1.71	1.66	4.919 gms.	0.266 gms.	0.532 gms.
1.188 gms.	1:2	1.14	1.09	3.230 "	0.414 "	1.242 "
	1:3	0.85	0.81	2.400 "	0.504 "	2.016 "
A/2	1:1	1.71	1.67	4.948 gms.	0.208 gms.	0.416 gms.
0.594 gms.	1:2	1.14	1.10	3.259 "	0.327 "	0.981 "
	1:3	0.85	0.82	2.430 "	0.384 "	1.536 "
A/3	1:1	1.71	1.68	4.978 gms.	0.148 gms.	0.296 gms.
0.396 gms.	1:2	1.14	1.11	3.289 "	0.237 "	0.711 "
	1:3	0.85	0.83	2.459 "	0.268 "	1.072 "
A/4	1:1	1.71	1.69	5.007 gms.	0.090 gms.	0.180 gms.
0.297 gms.	1:2	1.14	1.12	3.320 "	0.144 "	0.432 "
	1:3	0.85	0.84	2.489 "	0.148 "	0.592 "

TABLE III

Optically active substance used: Glucose.

Specific rotation of glucose taken = +51.34

50 mm. tube used.

Original rotation (β) = +1.80

Quantity of glucose per 100 c.c. of the solution = 7.012 gms.

Colloidal substance used: Arsenious hydrosulphide sol containing arsenic equivalent to 1.188 gms. of As_2O_3 per litre.

Equivalent quantity of As_2O_3 per litre.	Ratio of the original glucose solution to the sol.	Rotation expected on equation (II). $\left(\frac{\beta}{n+1}\right)$	Actual rotation observed. (β')	Quantity of glucose present per 100 c.c. of the mixed solution examined.	Quantity of glucose adsorbed per 100 c.c. of the mixed solution examined.	Quantity adsorbed pper 100 c.c. of the sol.
A/1	1:1	0.90	0.84	3.272 gms.	0.468 gms.	0.936 gms.
1.188 gms.	1:2	0.60	0.55	2.143 "	0.583 "	1.749 "
	1:3	0.45	0.41	1.597 "	0.624 "	2.496 "
A/2	1:1	0.90	0.85	3.311 gms.	0.390 gms.	0.780 gms.
0.594 gms.	1:2	0.60	0.56	2.182 "	0.466 "	1.398 "
	1:3	0.45	0.42	1.636 "	0.468 "	1.872 "
A/3	1:1	0.90	0.86	3.351 gms.	0.310 gms.	0.620 gms.
0.396 gms.	1:2	0.60	0.58	2.259 "	0.235 "	0.705 "
	1:3	0.45	0.43	1.675 "	0.312 "	1.248 "
A/4	1:1	0.90	0.87	3.389 gms.	0.234 gms.	0.468 gms.
0.297 gms.	1:2	0.60	0.56	2.182 "	0.466 "	1.398 "

TABLE IV

Optically active substance used: Galactose.
Specific rotation of galactose taken = +83.91

Original rotation (β) = +0.91
Quantity of galactose per 100 c.c. of the solution = 2.169 gms.

50 mm. tube used.

Colloidal substance used: Arsenious hydrosulphide sol containing arsenic equivalent to 1.188 gms. of As_2O_3 per litre.

Equivalent quantity of As_2O_3 per litre.	Ratio of the original galactose solution to the sol.	Rotation expected on equation (II). $\left(\frac{\beta}{n+1}\right)$	Actual rotation observed. (β')	Quantity of galactose per 100c.c. of the mixed solution examined.	Quantity of galactose adsorbed per 100 c.c. of the mixed solution examined.	Quantity adsorbed per 100 c.c. of the sol.
A/1	1:1	0.46	0.43	1.040 gms.	0.089 gms.	0.178 gms.
1.188 gms.	1:2	0.30	0.27	0.645 "	0.234 "	0.702 "
	1:3	0.23	0.20	0.477 "	0.261 "	1.044 "
A/2	1:1	0.46	0.44	1.049 gms.	0.071 gms.	0.142 gms.
0.594 gms.	1:3	0.30	0.28	0.667 "	0.168 "	0.504 "
	1:3	0.23	0.21	0.500 "	0.169 "	0.676 "
A/3	1:1	0.46	0.44	1.049 gms.	0.071 gms.	0.142 gms.
0.396 gms.	1:2	0.30	0.29	0.691 "	0.096 "	0.288 "
	1:3	0.23	0.21	0.500 "	0.169 "	0.676 "
A/4	1:2	0.30	0.29	0.691 gms.	0.096 gms.	0.288 gms.
0.297 gms.						

TABLE V

Optically active substance used: Sucrose. Original rotation $(\beta) = +15.71$
Specific rotation taken $= +67.5$ Quantity of sucrose per 100 c.c. of the solution = 10.579 gms.

220 mm. tube used.
Colloidal substance used: Antimony hydrosulphide sol containing antimony equivalent to 1.45 gms. of Sb_2O_3 per litre.

Equivalent quantity of Sb_2O_3 per litre.	Ratio of the original sucrose solution to the sol.	Rotation expected on equation (II). $\left(\frac{\beta}{n+1}\right)$	Actual rotation observed. (β')	Quantity of sucrose present per 100 c.c. of the mixed solution examined.	Quantity of sucrose adsorbed per 100 c.c. of the mixed solution examined.	Quantity adsorbed per 100 of the sol.
$B/2$	1:1	7.86	7.11	4.788 gms.	1.003 gms.	2.006 gms.
0.725 gms.	1:2	5.24	4.78	3.219 "	0.922 "	2.766 "
	1:3	3.93	3.60	2.424 "	0.883 "	3.532 "
$B/3$	1:1	7.86	7.21	4.855 gms.	0.869 gms.	1.738 gms.
0.483 gms.	1:2	5.24	4.82	3.245 "	0.844 "	2.532 "
	1:3	3.93	3.63	2.444 "	0.803 "	3.212 "
$B/4$	1:1	7.86	7.39	4.976 gms.	0.627 gms.	1.254 gms.
0.363 gms.	1:2	5.24	4.93	3.320 "	0.619 "	1.847 "
	1:3	3.93	3.73	2.512 "	0.531 "	2.124 "

TABLE VI

Optically active substance used: Glucose.
Specific rotation taken = +51.34

Original rotation (β) = +4.11
Quantity of glucose per 100 c.c. of the solution = 3.639 gms.

220 mm. tube used.
Colloidal substance used: Antimony hydrosulphide sol containing antimony equivalent to 1.45 gms. of Sb_2O_3 per litre.

Equivalent quantity of Sb_2O_3 per litre.	Ratio of the original glucose solution to the sol.	Rotation expected on equation (II). $\left(\frac{\beta}{n+1}\right)$	Actual rotation observed. (β')	Quantity of glucose present per 100 c.c. of the mixed solution examined.	Quantity of glucose adsorbed per 100 c.c. of the mixed solution examined.	Quantity adsorbed per 100 c.c. of the sol.
B/1	1:1	2.06	1.83	1.621 gms.	0.397 gms.	0.794 gms.
1.45 gms.	1:2	1.37	1.21	1.072 "	0.423 "	1.269 "
	1:3	1.03	0.86	0.762 "	0.591 "	2.369 "
B/2	1:1	2.06	1.85	1.639 gms.	0.361 gms.	0.722 gms.
0.725 gms.	1:3	1.03	0.94	0.832 "	0.311 "	1.244 "
B/3	1:1	2.06	1.91	1.691 gms.	0.257 gms.	0.514 gms.
0.483 gms.	1:2	1.37	1.26	1.116 "	0.291 "	0.873 "
	1:3	1.03	1.01	0.854 "	0.223 "	0.892 "
B/4	1:1	2.06	2.01	1.78 gms.	0.079 gms.	0.158 gms.
0.363 gms.	1:2	1.37	1.33	1.178 "	0.105 "	0.315 "
	1:3	1.03	1.01	0.854 "	0.223 "	0.892 "

TABLE VII

Optically active substance used: Galactose.
Specific rotation taken = +83.91

Original rotation = +2.42
Quantity of galactose per 100 c.c. of the solution = 1.311 gms.

220 mm. tube used.

Colloidal substance used: Antimony hydrosulphide sol containing antimony equivalent to 1.45 gms. of Sb_2O_3 per litre.

Equivalent quantity of Sb_2O_3 per litre.	Ratio of the original galactose solution to the sol.	Rotation expected on equation (II). $\left(\frac{\beta}{n+1}\right)$	Actual rotation observed. (β')	Quantity of galactose per 100 c.c. of the mixed solution examined.	Quantity of galactose adsorbed per 100 c.c. of the mixed solution examined.	Quantity adsorbed per 100 c.c. of the sol.
B/1 1.45 gms.	1:1	1.21	0.91	0.493 gms.	0.325 gms.	0.650 gms.
	1:2	0.81	0.61	0.331 "	0.318 "	0.954 "
	1:3	0.61	0.31	0.168 "	0.639 "	2.556 "
B/2 0.725 gms.	1:1	1.21	1.08	0.585 gms.	0.141 gms.	0.282 gms.
	1:2	0.81	0.71	0.383 "	0.156 "	0.468 "
	1:3	0.61	0.39	0.211 "	0.467 "	1.868 "
B/3 0.483 gms.	1:1	1.21	1.10	0.596 gms.	0.119 gms.	0.238 gms
	1:2	0.81	0.76	0.412 "	0.075 "	0.225 "
B/4 0.363 gms.	1:1	1.21	1.13	0.612 gms.	0.087 gms.	0.174 gms.
	1:2	0.81	0.76	0.412 "	0.075 "	0.225 "
	1:3	0.61	0.51	0.276 "	0.207 "	0.828 "

From the tables it is clear that the values of rotations observed are always less than the calculated ones i.e. $\beta' < \frac{\beta}{n+1}$ and these differences become more and more marked as the ratio of the sol to that of the sugar is increased. The other thing to be noted is that with the dilution of the solution this difference decreases. From these the possibility of the first theory mentioned in the introduction is excluded, and it becomes obvious that other factors besides those postulated by it are interfering.

But if the explanation of the phenomenon of protection, as put forward by Zsigmondy and Langmuir, be taken into account, it may be possible to explain this anomalous result. It is quite probable that this decrease in rotation is due to the fact that sugar molecules condensed on the surface of the particles are oriented in such a manner that they are no more optically active. That the optically active sugar has lost its optical activity in the adsorbed state is no wonder. It may be counted as one out of the many cases of chemical action between the protecting agent and colloid particles demonstrated by Zsigmondy, and theoretically postulated by Langmuir[1]. Just as in Zsigmondy's experiment the gelatin adsorbed by gold (loc. cit.) lost its property of solution in water, so also the sugar might have undergone changes in physical and chemical properties.

TABLE VIII

All the values of rotations given in this table are positive.

Initial rotation due to the mixture of the sol and sugar solution.	Rotation of the solution got by dissolving the coagulum.
1.66	nil
1.10	nil
0.84	nil
0.43	nil
7.11	nil
4.93	nil

To test this, in each case, the particles were coagulated and after washing twice or thrice to get rid of the mechanically adhering sugar the coagula were dissolved in alkali or acid as required and the rotation examined.

It must be noted that it is not possible to wash off the adsorbed substance as the experiments of Whitney and Ober[2] have shown, so that there is no danger of the adsorbed sugar being lost in two or three washings. The presence of elements constituting sugar molecule has been established later by an actual chemical analysis. Some of the results of the previous experiments are given in Table VIII.

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[1] J. Am. Chem. Soc. 39, 1848 (1917).

[2] J. Am. Chem. Soc. 23, 342 (1901).

The above results show conclusively that the amount of sugar adsorbed has lost its optical activity. Thus the chemical theory is amply supported. Further support has been found by a qualitative chemical analysis of the adsorbent, as shown later on. It is evident that in this particular case muta-rotation is not the factor interfering as it is not a decrease or increase in the optical rotation that is observed but a total extinction of the property. It must also be noted that the rotations are sufficient to denote any small decrease or increase in the polarimeter used, the instrument being sufficiently accurate and sensitive.

In order to see if there were other cases as above, many experiments with different adsorbents and optically active substances were tried. Fine powders of substances like arsenic trisulphide, zinc oxide, ferric oxide, anthracene, β-napthol and such others were used as adsorbents. The method of experimentation was as follows:—

A solution of the optically active substance was prepared and measured quantities of this were put in glass stoppered flasks. Weighed amounts of adsorbents to be experimented upon were put in different bottles, and the original solution was put in a separate bottle. After a few hours the rotations due to the original solution as also those due to the solutions obtained by filtering, were examined. Special care was taken in filtering, filter papers being soaked for some time in the original solution of the optically active substance, and then dried after thoroughly washing.

It is interesting to note that the rotations of the optically active substance, were affected to any measurable amount by only those substances which adsorb. Substances like anthracene, β-napthol did not produce any change in the rotation even when kept over night with the solution of the active subtance. The results of the experiments with ammonium tartrate and arsenic trisulphide powder are given in Tables IX and X.

Observations made with other adsorbents and optically active sugars are in the same direction as the above. These results clearly prove the conclusions arrived at before, namely, that on account of some chemical action between the adsorbent and the adsorbed optically active substance, the amount of the active substance adsorbed has lost its activity.

Further to show the presence of the adsorbed sugar in the washed adsorbent following experiments were done with zinc oxide and glucose: some zinc oxide after being put for some time with the glucose solution, was taken out and washed three or four times. It was then dried, and a portion of it was dissolved and glucose was tested for in the solution by means of Pavy's solution. No test of glucose was found. The other portion of the zinc oxide, supposed to have adsorbed glucose was mixed with finely powdered copper oxide and heated in a combustion tubing to test qualitatively for carbon. With this

TABLE IX

Optically active substance used: Ammonium tartrate.
Quantity taken 3.2933 gms. Original rotation with 220 mm. tube = +2.41
Specific rotation = +33.26

Substance examined: Merck's arsenic trisulphide.

Observations on polarimeter taken one hour after the addition of ammonium tartrate to the arsenic trisulphide.

Mass of arsenic tri-sulphide.	Volume of ammonium tartrate solution added.	Quantity of ammonium tartrate before ad-sorption.	Rotation after adsorption.	Quantity of ammonium tartrate after ad-sorption.	Quantity adsorbed.	Rotation in the solution obtained by dissolving the washed adsorbent in alkali.
1.8572 gms.	50 c.c.	1.65 gms.	2.11	1.44 gms.	0.21 gms.	nil.
2.9411 "	50 c.c.	0.83 "	1.06	0.73 "	0.10 "	nil.
1.5903 "	60 c.c.	1.98 "	2.28	1.87 "	0.11 "	nil.
3.5584 "	40 c.c.	1.27 "	2.04	1.12 "	0.15 "	nil.

TABLE X

Optically active substance used: Ammonium tartrate.

220 mm. tube used. Specific rotation = +33.26

Substance used as adsorbent: Merck's arsenic trisulphide.

Observations on polarimeter taken three hours after the addition of ammonium tartrate to the arsenic trisulphide.

Mass of arsenic tri-sulphide.	Volume of ammonium tartrate solution added.	Quantity of ammonium tartrate before ad-sorption.	Rotation after adsorption.	Quantity of ammonium tartrate after ad-sorption.	Quantity adsorbed.	Rotation in the solution obtained by dissolving the washed adsorbent in alkali.
1.5610 gms.	25 c.c.	0.962 gms.	2.35	0.803 gms.	0.159 gms.	nil.
2.6008 "	30 c.c.	1.1541 "	2.38	0.975 "	0.179 "	nil.
2.0478 "	40 c.c.	1.5388 "	2.43	1.328 "	0.211 "	nil.
3.9290 "	50 c.c.	1.9235 "	2.42	1.654 "	0.270 "	nil.
4.2218 "	60 c.c.	2.3082 "	2.45	1.949 "	0.359 "	nil.

another blank experiment with zinc oxide was made for the sake of comparison. It was found that the former showed the presence of carbon. These two experiments have clearly demonstrated the loss of the chemical property of glucose in the adsorbed state, as also the presence of some carbon compound on the adsorbent.

The above observations are striking, but further work is necessary so that the views developed here can be finally accepted. In order to get more evidence in this direction experiments with adsorbents like zinc oleate, zinc stearate, aluminium palmitate, etc., soluble in alcohol, ether, and other organic solvents are in progress in this laboratory.

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THE REDUCTION OF FREE NITRIC ACID BY MEANS OF FERROUS STANNOUS, OR TITANOUS SALTS

BY LOWELL H. MILLIGAN[1] AND G. RAYMOND GILLETTE[2]

I. Introduction

The results presented in this paper, which is one of a series from the Laboratory of Chemistry of Cornell University, contribute toward an investigation of the action of nitric acid on metals or, in more general terms, the mechanism of the reduction of nitric acid. The subject is one which has interested investigators since the beginnings of our science of chemistry, but in spite of the early origin of the problem and in spite of much intensive work directed toward its solution a completely satisfactory theory has not yet been developed.

In a previous paper by one of us[3], methods of analysis are described for the reduction products of free nitric acid solutions, namely—nitrogen peroxide, nitric oxide, nitrous oxide, nitrogen, nitrous acid, and salts of hydroxylamine, hydrazine and ammonia. The present paper gives results which were obtained when a study was made of the reduction of nitric acid by means of ferrous, stannous, or titanous salts, using these analytical methods. Part of the development work on the methods was done in connection with reduction experiments, and therefore the analytical accuracy obtained, as shown by the summation of reducing agent accounted for compared with that added, is not always quite so satisfactory as would have been the case if the methods finally adopted had been uniformly applied, but is believed to be sufficient for the present purpose. The work was carried out under the general direction of Prof. Wilder D. Bancroft.

II. The Reduction of Free Nitric Acid by Means of Ferrous Salts

When small amounts of nitric acid are added to an excess of ferrous chloride solution containing free hydrochloric acid, and the mixture is boiled in the absence of air, the nitric acid is quantitatively reduced to nitric oxide which is expelled from the boiling solution; and this procedure has been made the basis of a method for the quantitative determination of nitrates.[4]

With low concentrations of ferrous ion and nitric acid at room temperature, the reaction takes place with extreme slowness, but there does not appear to be a limiting concentration below which some reaction will not occur. Strong ferrous sulphate solutions containing a few drops of nitric acid will remain a light green color for a long time, but eventually (months) will turn red-brown,

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[1] Holder of the duPont Fellowship in Chemistry at Cornell University for 1922-23.

[2] Senior in chemistry at Cornell University in 1922-23.

[3] Lowell H. Milligan: Jour. Phys. Chem., 28, 529 (1924).

[4] Method of Schloesing and Grandeau, modified by Tiemann and Schulze: Zeit. anal. Chem., 9, 401 (1870); Ber., 6, 1041 (1873).

indicating the formation of nitric oxide which combines with the ferrous sulphate to give the same more or less unstable complex compound[1] which results when nitric oxide is passed into cold ferrous sulphate solution.

Boiling the ferrous sulphate—nitric acid solution accelerates the reaction and renders the complex compound unstable, at once expelling nitric oxide.

Experiments were made to determine the reactions taking place when ferrous sulphate solutions were treated with an excess of free nitric acid. When 35% nitric acid is added in large excess to a strong solution of ferrous sulphate at room temperature, so that the final mixture contains about 20 gms. of nitric acid per 100 cc of solution, no evidences of reaction appear for a while. Then, suddenly, the dark red-brown color indicative of the ferrous sulphate—nitric oxide complex appears at one spot and spreads rapidly throughout the whole solution. This condition persists only for a few minutes, however, and then the color bleaches rapidly to a light yellow-green with an attendant formation of small bubbles of gas. These phenomena are interpreted to represent: first an induction period; second the formation of nitrous acid and nitric oxide according to the reactions,

$$2FeSO_4+HNO_3+H_2SO_4=Fe_2(SO_4)_3+HNO_2+H_2O$$
$$3HNO_2=HNO_3+2NO+H_2O$$

and combination of the nitric oxide with the ferrous sulphate to give the red-brown color; and third the decomposition of this complex compound with evolution of the nitric oxide, due to the fact that diminishing ferrous sulphate concentration and rising temperature (from the heat of reaction) have rendered it unstable.

It is not improbable that the reaction goes through other unstable intermediate stages. The hypothetical compound $H_2N_2O_5$, of which N_2O_4 is the anhydride, is quite likely to be the first reduction product, and Angeli's nitrohydroxylamic acid ($H_2N_2O_3$) probably stands between nitrous acid and nitric oxide.

When a considerable amount of sulphuric acid has been added to the reaction mixture the period of induction is especially notable, and in this event the addition of a small quantity of nitrous acid seemed to act as a positive catalyzer.

The results of quantitative experiments are given in Table I. These were carried out in an atmosphere of pure carbon dioxide, and the analyses of the products were made substantially as described in the previous paper. The total reducing power of the undecomposed ferrous sulphate and the nitrous acid was titrated with standard permanganate, and nitrous acid was estimated colorimetrically by means of the metaphenylenediamine reaction. Known amounts of standard sodium nitrite solution were added to a colorimetric comparison sample containing the same original materials as were in the unknown but diluted to the point where the rate of reaction was negligible. Only a very small amount of nitrous acid was found and it has been calculated to nitric oxide and added to the nitric oxide which was given off as a gas.

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[1] See, for instance, Schlesinger and Salathe: J. Am. Chem. Soc. 45, 1871 (1923).

In these experiments the concentrations are such that the red-brown color appears and disappears within half an hour after mixing the solutions at 20°C. Nitric oxide is the chief product, but nitrogen peroxide is also always present. No nitrogen, nitrous oxide, hydroxylamine or ammonia is formed. Neither the presence of sulphuric acid nor the time during which the products are left in contact with the reacting solution has any special directive influence on the reaction. More concentrated nitric acid would undoubtedly increase the amount of nitrogen peroxide formed.

TABLE I

The Reduction of Nitric Acid by Means of Ferrous Sulphate at 20°C. (From 7 to 17 times the amount of HNO_3 which would be required by the $FeSO_4$ to produce NO_2 has been used in these experiments.)

Exp. No.	Composition of original solution. Gms per 100 cc.			Time between making the solution and analysis; hours.	Per cent $FeSO_4$ accounted for as			
	$FeSO_4$	HNO_3	H_2SO_4		NO	NO_2	Unoxidized $FeSO_4$	Loss
1	2.76	19.4	0.0	0.5	67.8	5.09	25.4	1.71
2	3.79	14.6	20.5	0.5	66.0	4.99	24.0	5.01
3	3.66	15.2	19.9	0.5	60.9	4.88	29.5	4.72
4	4.41	12.1	23.9	20.	75.2	5.08	18.2	1.52

The loss is mainly due to the fact that the reaction is slow because the reaction flask was not heated, and oxides of nitrogen were given off continuously during the analysis. It was therefore impossible to wash the gases quantitatively with the carbon dioxide stream into the absorbing liquids, and those oxides of nitrogen which were not absorbed were lost when the apparatus was taken apart. When sulphuric acid is present in the reacting mixture the oxides of nitrogen are evolved still more slowly and under these conditions if the analysis is begun immediately after the red-brown color has disappeared, the loss is greater. When considerable time elapses between the beginning of the reaction and the analysis, as in No. 4, the loss is less.

III. The Reduction of Nitric Acid by Means of Stannous Salts

Maumené[1] treated nitrates with stannous chloride in acid solution, and obtained crystalline hydroxylamine hydrochloride from the solution.

Dumreicher[2] found that nitric oxide was completely absorbed by a hydrochloric acid solution of stannous chloride at 100°C with the formation of ammonium salts. Pure hydroxylamine hydrochloride was likewise reduced to ammonium salts, and the reaction was quantitative. He could not detect any action between nitrous oxide and stannous chloride even after standing a week. With nitrous acid and stannous chloride solution he obtained nitrous

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[1] Compt. rend. **70**, 147 (1870).

[2] Monatshefte, **1**, 724 (1880).

oxide alone in dilute solutions, or nitrous oxide plus red oxides of nitrogen if the solution was concentrated, but he did not find any free nitrogen in either case. Nitric acid added to stannous chloride solution gave only a slow reaction in the cold with the formation of some hydroxylamine and ammonium salts; in the hot, considerable amounts of ammonium salts were produced.

Divers and Haga[1] disagreed with some of Dumreicher's conclusions. They found that in the absence of air the products of reaction between nitric oxide and stannous chloride solution were hydroxylamine salts and nitrogen, but not ammonium salts. With nitric acid and stannous chloride they obtained no reaction in cold dilute solutions, but hydroxylamine salts resulted when the solutions were more concentrated.

The statements of different authors, while probably correct in the main, sometimes conflict, and are not always convincing because their analytical work was not complete and the methods used were not, in general, capable of yielding very accurate results.

In order to get an idea of the general behavior of stannous chloride solutions when treated with an excess of nitric acid, experiments were made by mixing these reagents either with or without the addition of sulphuric acid, and the mixtures were warmed up in a water bath until decomposition took place. This began spontaneously at a fairly definite temperature, as shown by violent bubbling, the development of a yellow color in the solution starting at the top and working downward, and the evolution of light brownish-colored fumes. This temperature was noted as being a measure of the stability of the solution or an inverse measure of the rate of reaction. On this basis it was found, as would be expected from the mass law, that increasing the concentration of the nitric acid or stannous chloride lowered the decomposition temperature. Increasing the concentration of sulphuric acid in a solution in which the concentration of nitric acid and stannous chloride were kept constant, also lowered the decomposition temperature, serving to increase the *effective* concentration of the solution. Thus a solution containing 15 gm $SnCl_2$, 6 gm HCl, 25 gm HNO_3 and 22.7 gm H_2SO_4 per 100 cc, decomposed at 64°C under a definite set of conditions, but when the H_2SO_4 content of this same solution was raised to 60.5 gm the decomposition temperature was lowered to 32°.

It was found that concentrated (70%) nitric acid could be added to a stannous chloride solution (made by letting concentrated hydrochloric acid (39%) react with as much tin as it would dissolve at room temperature) without producing any visible reaction, provided the solutions were brought to —15°C and were mixed slowly with intermediate cooling in an ice-salt mixture. Data on such a solution and also one which was slightly more dilute, are given in Table II.

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[1] J. Chem. Soc., **47**, 623 (1885).

The total reducing power of these solutions was determined by the hypochlorite method, and the free $SnCl_2$ by the iodine titration method, the NH_2OH being calculated from the difference between these titrations.

TABLE II

The Action of an Excess of Strong Nitric Acid on Stannous Chloride Solution.

	Gms. per 100 cc at 20°C.			
	$SnCl_2$	HCl	HNO_3	NH_2OH (calc. to equiv. $SnCl_2$)
Solution A				
Original at −15°C.	30.	12.	50.	none
10 min at −15°	28.5	—	—	1.5
9 min after bringing to 20°	12.6	—	—	18.0
10 min after bringing to 20°	Spontaneous decomposition, raising the temp. to 50° and giving off brownish fumes.			
Solution B				
Original	20.	8.	27.	none
4 hrs at 20° (no change in appearance)	6.74	—	—	12.96

In order to trace the formation of hydroxylamine and ammonium salts in solutions containing stannous chloride and a large excess of free nitric acid, the series of solutions given in Table III were made up by mixing ice cold reagents and then letting them warm up to room temperature in an atmosphere of neutral gas (hydrogen in the first three cases, and carbon dioxide in the fourth). The behavior and analyses of these solutions are given in the notes to Tables III, IV and V, and in Fig. 1. In Fig. 1 it is seen that the points obtained were insufficient to define the curves with any great degree of accuracy, but their general trend is unmistakable. In Tables 4 and 5 the "$SnCl_2$ not accounted for" may be partly a loss due to oxidation by the air, which was not completely excluded while the samples were being taken. The analytical methods for $SnCl_2$ and NH_2OH are given in the preceding paragraph. Analyses for ammonia, made by the distillation method, showed none present in any case.

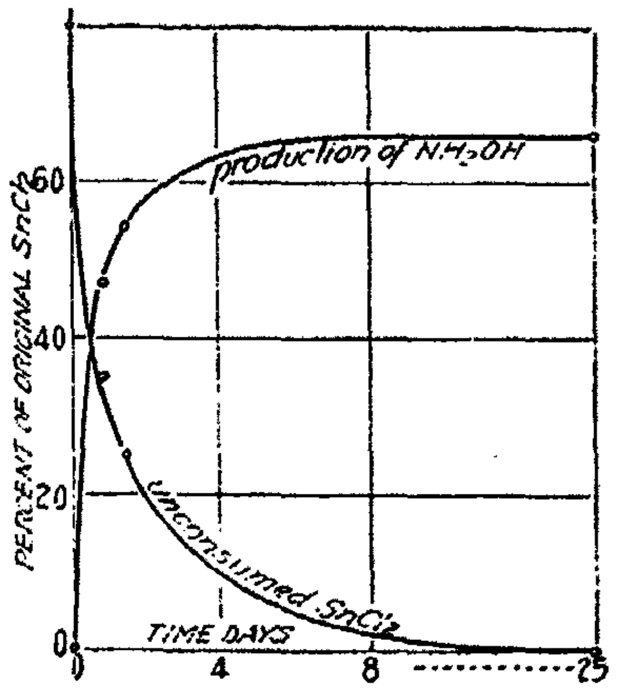

FIG. 1.

Curves showing how the production of NH_2OH and the unconsumed $SnCl_2$ varied with time for solution no. 3.

Behavior of Solutions

Soln. 1. Warmed rapidly up to about 5°C above room temperature. Titration made five minutes after mixing showed no stannous tin present, although no gas was given off and there had been no change in the appearance of the solution. Twenty minutes after mixing, the solution suddenly turned yellow and a violent evolution of brownish gas occurred.

Table III

Composition of Solutions used for Experiments.

Soln. No.	Gms reagent per 100 cc soln.			
	HNO_3	HCl	$SnCl_2$	H_2SO_4
1	23.3	9.9	8.3	0.
2	13.6	4.1	9.6	45.4
3	16.3	5.0	11.6	0.
4	20.4	4.8	12.0	0.

Soln. 2. Warmed rapidly up to about 5°C above room temperature. Titration made five minutes after mixing showed stannous tin present equivalent to 3.5 gm $SnCl_2$ per 100 cc solution, or 36% of the amount originally present. During the night (between two and eighteen hours after mixing) evolution of brownish gas occurred, and in the morning the solution was light yellow. Titration showed no stannous tin present.

Solns. 3 and 4. Warmed up slightly, but did not change in appearance during the total time of observation. (See Tables IV and V and Fig. 1.)

Table IV

Analyses of Solution 3, Table III

Elapsed Time	$SnCl_2$ found		NH_2OH found (expressed as equiv. $SnCl_2$)		NH_3 found	$SnCl_2$ not accounted for
	Gm/100cc	% of original	Gm/100cc	% of orig. $SnCl_2$		% of orig. $SnCl_2$
5 min.	11.4	98.	—	—	—	—
23 hrs.	4.02	34.6	5.55	46.9	—	18.5
36 hrs.	2.93	24.8	6.20	53.6	—	21.6
25 days	0.00	0.0	7.62	65.8	none	34.2

Table V

Analyses of Solution 4, Table III

2.5 hrs.	9.72	81.2	2.18	18.3	—	0.5
6.5 hrs.	7.90	66.1	3.61	30.2	—	3.7
18.5 hrs.	5.48	45.8	5.21	43.6	none	10.6

Experiments were also made using a considerable excess of stannous chloride over that required by the nitric acid present. The data are given in Table VI. The amount of $SnCl_2$ used is an excess of 124% over the amount required to convert the HNO_3 present into NH_2OH, or 69% over the amount required to convert it into ammonia.

No visible signs of reaction appeared. The sum of the hydroxylamine and ammonia was determined by the titanous salt method, the ammonia was determined by distillation and the hydroxylamine was calculated by difference.

The preceding experiments indicate that when stannous chloride solutions are treated with an excess of nitric acid, hydroxylamine salts are the first end-reduction product produced in the solution; but that the hydroxylamine salts are often oxidized to gaseous products if the concentration of nitric acid is sufficiently great. When stannous chloride is in excess, at least a part of the hydroxylamine is reduced to ammonium salts.

Table VI

The Reduction of Free Nitric Acid by Means of an Excess of Stannous Chloride Solution

	Gms per 100 cc.				
	$SnCl_2$	HCl	HNO_3	NH_2OH (calc. as $SnCl_2$)	NH_3 (calc. as $SnCl_2$)
Original solution	61.3	23.4	3.02	none	none
Standing at 20°C for 30 min.	61.3	——	——	none	none
Portion heated to 95°C for 10 min.	——	——	——	10.0	12.7
Portion Standing at 20° for 25 days	——	——	——	7.2	6.5

If this is the true mechanism of the reaction, and the presence of the tin ions have no specific catalytic effect, then the gaseous products given off when nitric acid is added in excess to stannous chloride solutions should be the same as those produced when excess nitric acid is added to solutions of hydroxylamine salts. The experiments given in Table VII were made to test this point, and these confirm the mechanism postulated for the reaction. The fact that small amounts of NO_2, NO, and N_2 accompany the production of N_2O as the main product when hydroxylamine salts are oxidized with nitric acid seems to the writers to indicate that the reaction goes through unstable intermediate stages. On this basis the fact that hydroxylamine *alone* seems to be the *primary* end-reduction product between stannous chloride solutions and an excess of nitric acid, would be interpreted to mean that the concentration of the intermediate stages under these conditions never reaches the point where decomposition to gaseous products takes place.

One experiment was made exactly like No. 5 in Table VII except that 0.25 gm of $CuSO_4$ also was present per 100 cc of the original solution. This had no directive effect on the reaction, and the results obtained were practically like those given in the table. This is interpreted to mean that cupric salt is not a catalyzer for the production of nitric oxide under these conditions. Nothing, however, can be said about what the effect of cuprous salt would be, provided it could be kept present as such during the reaction.

TABLE VII

Reduction of an Excess of Free Nitric Acid with a Solution of Stannous Chloride, or Hydroxylamine Hydrochloride or Hydrosulphate.

Exp. No.	Composition of soln. taken; gm./100 cc.					Max. Temp., °C	React Time, hrs.	Reaction products found; calc. as equiv. $SnCl_2$ and expressed as % of total taken.							
	$SnCl_2$ added	NH_2OH calc. as equiv. $SnCl_2$	HNO_3	H_2SO_4	HCl			NO_2	NO	N_2O	N_2	NH_2OH	NH_3	Undecomp. $SnCl_2$	Total
1	10.70*	——	12.6	0.0	13.6	20	13	0.0	0.0	0.0	0.0	13.3*	0.0	82.9*	96.2*
2	6.91	——	10.2	55.2	2.07	90	1	0.15	0.99	93.3	5.0	0.0	0.0	0.0	99.4
3	——	4.385	10.2	55.2	2.52	90	1	——**	——**	97.3	0.0	0.0	0.0	——	——**
4	——	4.59	20.7	0.40	0.0	80	0.5	0.26	5.66	91.5	3.4	0.0	0.0	——	100.8
5	——	4.59	31.2	0.40	0.0	70	0.5	0.26	2.37	93.5	2.1	0.0	0.0	——	98.2
6	——	3.64	43.7	0.32	0.0	60	0.5	0.34	1.37	91.9	5.3	0.0	0.0	——	98.8

*In experiment No. 1 the total reducing power of the solution was determined by diluting a 10 cc sample to 800 cc and titrating with standard I_2 solution, and the NH_2OH was determined by the NaBrO method. This accounts for the low percent recovery given in the last column because these procedures give low results, as described in the previous paper, due to loss of stannous salt by oxidation with dissolved air in the first case, and to incomplete reaction in the second. The analytical methods used for the rest of the experiments were those which have been shown to give correct results.

**In experiment No. 3 some of the chloride in the solution was oxidized to gaseous chlorine compounds which were absorbed in the reagents used for NO_2 and NO, and rendered these determinations valueless. The gaseous chlorine compounds were detected by their odor, and when the sulfuric acid in the first absorption bottle was analyzed, the "total nitrogen" indicated by nitrometer was found to be less than the "nitrous nitrogen" determined by permanganate titration.

IV. The Reduction of Nitric Acid by Means of Titanous Salts

Titanous salts are stronger reducing agents in acid solutions than are corresponding stannous salts, as shown both by electromotive force measurements[1] and by reduction experiments[2].

It has just been shown that stannous salts reduce nitric acid to hydroxylamine and eventually to ammonium salts, and therefore it would be expected, reasoning purely from the apparent reducing strength of the solutions, that ammonium salts would be the chief reduction product with titanous salts and nitric acid; but, on the contrary, nitric oxide is mainly formed. When, for instance, a few drops of titanous chloride solution are added to 20% nitric acid, an instantaneous evolution of gas occurs and analysis shows it to be more than 50% nitric oxide. If stannous chloride were used under these same conditions there would be no obvious reaction, but hydroxylamine salts would be slowly formed in the solution. In terms of the reaction mechanism previously postulated, this is interpreted to mean that titanous salts exert a specific catalytic effect on the decomposition of nitrohydroxylamic acid, producing nitric oxide in quantity before much of the nitrohydroxylamic acid has a chance to be further reduced.

Only two quantitative experiments were made using titanous chloride to reduce nitric acid, because of lack of available time. The results given in Table VIII, while perfectly definite, nevertheless fail to account for the entire amount of the titanous salt taken. This is due to the fact that the experiments were made at room temperature and it was assumed at that time that the carbon dioxide passing through the solution would decompose the nitrous acid and wash out the nitric oxide. This was subsequently shown to be a wrong assumption[3], and accounts for the extremely high loss in Experiment No. 1. Experiment No. 2 was made in a similar way except that a permanganate titration (which could not be made with great accuracy because of the fading end-point, but is likely to be only a little low) was made on the residual liquid in the decomposition flask and the results were calculated to NO (after correcting for the small amount of hydroxylamine indicated to be present by the titanous salt method) and added to that collected in the absorption bottles. The total result obtained in this way is considerably better.

No complete experiments were made in which dilute nitric acid was added to an excess of titanous chloride solution, but experiments in connection with the development of the titanous salt method for the determination of hydroxylamine[4] showed that ammonium salts are not a product under these conditions. This, and other phenomena noticed in those experiments, indicates that the reaction proceeds to practically the same products with titanous salt and nitric acid no matter which constituent is in excess. Support is thereby sup-

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[1] Foerster: "Elektrochemie wässeriger Lösungen" 217 (1922).

[2] Knecht and Hibbert: Ber., 36, 166, 1549 (1903); 38, 3318 (1905); Stähler: Ber., 42, 2695 (1909); Bray, Simpson and MacKenzie: J. Am. Chem. Soc., 41, 1363 (1919).

[3] See discussion under nitrous acid in the paper on analytical methods.

[4] See previous paper on analytical methods. J. Phys. Chem. 28, 544 (1924).

plied to the view that the "ous" salt of titanium is the catalytic agent causing the decomposition of nitrohydroxylamic acid and splitting off of nitric oxide. Further confirmation was obtained by adding titanic salt to a solution containing nitric acid and stannous chloride, in which case the reaction did not appear to be affected, and nitric oxide did not split off preferentially as should have been the case if the "ic" salt of titanium were the catalyzer.

TABLE VIII

Reduction of an Excess of Free Nitric Acid with a Solution of Titanous Chloride

Maximum temp. 20°; time of reaction 10 minutes; no ammonia formed

Composition of soln. taken; gm/100cc			React. products formed; calc. to equiv. $TiCl_3$ and expressed as % of total taken					
$TiCl_3$	HNO_3	H_2SO_4	NO_2	NO	N_2O	N_2	NH_2OH	Total
5.99	5.82	0.0	1.55	55.3	22.5	2.55	1.15	83.0*
5.05	5.80	4.23	1.69	67.0	25.25	3.01	0.75	97.7*

*See discussion given in the text regarding these low totals.

V. Summary and Conclusions

The conclusions of this paper are:

1. When an excess of nitric acid of 15-20% strength is reduced at 20°C by ferrous salt solutions, first the reaction passes through an induction period and then the solution becomes dark red-brown indicative of the formation of the $Fe^{++}.NO$ complex which is rapidly decomposed, nitric oxide being the principal product but considerable nitrogen peroxide being formed also. When small amounts of nitric acid are added to an excess of boiling ferrous salt solution, nitric oxide only is produced.

2. When an excess of nitric acid of 10-50% strength is treated in the cold with stannous salt solutions, hydroxylamine salts are the *primary* end-product of the reaction, but when the conditions of temperature and concentration are such that the nitric acid and the hydroxylamine salts react, then nitrous oxide is the chief product together with small amounts of nitric oxide, nitrogen and traces of nitrogen peroxide. No ammonium salts are formed. When stannous salts are used in excess over the nitric acid, the reaction takes place with hydroxylamine and ammonium salts as the products either in hot or cold solutions, but the reaction is very slow in the latter case.

3. When an excess of nitric acid is treated with titanous salt solutions, the reaction takes place very rapidly with the formation of nitric oxide as the chief product together with a considerable amount of nitrous oxide, a smaller amount of nitrogen, and traces of nitrogen peroxide and also of hydroxylamine salts. No ammonium salts are formed. The reaction appears to progress in practically the same way no matter whether the nitric acid or the titanous salt is in excess, neither hydroxylamine nor ammonium salts being formed in the latter case.

4. Titanous salts are stronger reducing agents than corresponding stannous salts and yet the chief product produced by the former acting on an excess nitric acid is nitric oxide; whereas the chief product from the latter is hydroxylamine, which is a 'more reduced' compound but is produced by the weaker reagent. This shows that catalytic effects play an important part, and evidence indicates that the 'ous' salt of titanium is the catalyzer for the decomposition of nitrohydroxylamic acid and production of nitric oxide.

5. The mechanism given in Fig. 2 is suggested to represent the reduction of nitric acid. It applies also to reactions involving the other products shown.

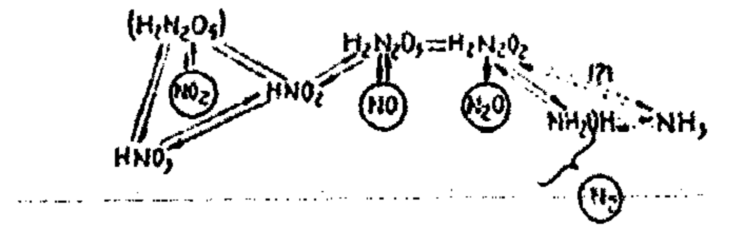

FIG. 2.
The mechanism of the reduction of nitric acid.

In this arrangement the gases are designated by enclosing them in circles. The vertical position of the rest of the compounds is chosen so as to indicate their approximate stability, those placed lowest down being most stable. The double arrows indicate that the reactions may proceed in either direction with appreciable velocity. Thus, on the one hand, concentrated nitric acid turns red on standing, due to the formation of red oxides of nitrogen; and, on the other, nitrogen peroxide is absorbed by water with the formation of nitric acid, nitrous acid and nitric oxide. Nitrogen and nitrous oxide are found as decomposition products in nitric oxide which has stood over water for some time, and so forth. Nitrous oxide and nitrogen are so relatively stable in the ordinary non-ionized form that they are represented with single arrows to indicate that they are end-products.

Nitrogen is evidently a product of reaction between hydroxylamine and one or more of the more-oxidized compounds. Kurtenacker and Neusser[1] believe that nitrogen is produced by the interaction of hydroxylamine with nitroxyl (NOH, considered to be a very reactive compound of which $H_2N_2O_2$ is a polymer). The arrows shown in Fig. 2 in connection with ammonia are dotted, because it is not certain just what the relationships are in this case.

Other equilibria are not shown on this diagram because it is thought that they complicate matters unnecessarily. These are:

$$\begin{array}{ll} 2NO_2 & \rightleftarrows N_2O_4 \\ NO_2+NO & \rightleftarrows N_2O_3 \\ 2HNO_3 & \rightleftarrows N_2O_5+H_2O \\ 2NOH & \rightleftarrows H_2N_2O_2 \end{array}$$

In alkaline solutions, stability relations are altered and the course of the reduction in any case is likely to be somewhat changed. This effect, in general applies both to the reducing agent used and to the nitrogen compounds. In

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[1] Z. anorg. Chem., **131**, 27 (1923), (through C. A. **18**, 796).

connection with the latter, salts of HNO_2, $H_2N_2O_3$ and $H_2N_2O_2$ are more stable than the free acids, and therefore a low hydrogen ion concentration in the solution tends to favor their formation.

In special solvents, new stability relations may be set up. Thus nitrosylsulphuric acid formed from nitrous acid (or nitrogen trioxide) and a large excess of concentrated sulphuric acid, according to the reaction

$$HNO_2+H_2SO_4 \longrightarrow NOHSO_4+H_2O,$$

may be considered to be simply nitrous acid stabilized by solution in concentrated sulphuric acid. When solid nitrosylsulphuric acid crystallizes from the solution, it is simply that the system has become super-saturated with respect to this particular compound, under the conditions of the experiment. Dilution of the sulphuric acid with water decreases the stability of the nitrosyl-sulphuric acid; nitrous acid is re-formed, and is decomposed at least partially into nitric oxide and nitric acid.

The presence of compounds which catalyze preferentially the decomposition of one or more of the primary products will have a specific directive influence on the reaction, independent of effects otherwise indicated by the relative strength of the reducing agent as shown by E. M. F. measurements or by other reactions. When the reaction in a given case passes rapidly through any of the unstable intermediate compounds, only very small quantities of the gases formed by their decomposition will result.

In order to be of any value, a theory should correlate and explain existing facts, and predict new ones. The existing general information from the literature or from this work on the reactions which these compounds undergo in aqueous solution is given in reaction form below.

(*a*) *Decompositions and interreactions of the nitrogen compounds.*

$$2NO_2+H_2O \longrightarrow HNO_3+HNO_2.$$

$$3HNO_2 \longrightarrow HNO_3+2NO+H_2O.$$

$$NO+H_2O \xrightarrow[\text{(slowly)}]{\text{(dark)}} HNO_2+N_2+(\text{a little } N_2O).$$

$$H_2N_2O_3 \longrightarrow 2NO+H_2O.$$

$$2Na_2N_2O_3+H_2O\ (\text{boil}) \longrightarrow 2NaNO_2+N_2O+2NaOH.$$

$$H_2N_2O_2 \longrightarrow N_2O+H_2O.$$

$$\underset{\text{(free liquid)}}{NH_2OH} \longrightarrow NO_2+NO+N_2+N_2O+NH_3.$$

(presence of Pt-black increases the N_2O)

(*b*) *Effect of adding oxidizing or reducing agents.*

$$KNO_3+\text{Na amalg.} \longrightarrow KNO_2 \longrightarrow NH_2OH+K_2N_2O_2.$$

$$\left.\begin{array}{l}KNO_2\\ \text{or } NO\end{array}\right\} + \left\{\begin{array}{l}Fe(OH)_2 \text{ or}\\ Sn(OH)_2\end{array}\right\} + KOH \longrightarrow K_2N_2O_2 + N_2O + N_2 + NH_3.$$

$$2HNO_2 + CO(NH_2)_2 \text{ (excess)} \longrightarrow 2N_2 + CO_2 + 3H_2O.$$

$$\begin{array}{l}NaNO_2 + NH_2OH.HCl \text{ (excess)} \longrightarrow H_2N_2O_2 + NaCl + 2H_2O.\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow\\ \qquad\qquad\qquad\qquad\qquad\qquad\quad N_2O + H_2O.\end{array}$$

$$\left.\begin{array}{l}HNO_3\text{, or}\\ HNO_2\end{array}\right\} + \left\{\begin{array}{l}SO_2\text{, or}\\ H_2S\end{array}\right. \longrightarrow NH_2OH.$$

$$\left.\begin{array}{l}HNO_3\text{, or}\\ NO\end{array}\right\} + Sn + HCl \text{ (excess)} \longrightarrow NH_2OH.HCl + NH_4Cl.$$

$$\left.\begin{array}{l}HNO_2\text{, or}\\ HNO_3\end{array}\right\} + Fe^{++} \left\{\begin{array}{l}\text{excess acid} \longrightarrow NO + NO_2.\\ \text{excess } Fe^{++} \longrightarrow NO.\end{array}\right.$$

$$HNO_3 \text{ (excess)} + Ti^{+++} \longrightarrow NO + N_2O + N_2 (+NO_2 + NH_2OH).$$

$$\left.\begin{array}{l}HNO_3\text{, or}\\ HNO_2\end{array}\right\} \begin{array}{l}+Hg + \text{conc.} H_2SO_4 \longrightarrow NO.\\ \text{(excess)}\end{array}$$

$$2KNO_3 + 6\ HCOOH \longrightarrow N_2O + 4CO_2 + 5H_2O + 2HCOOK.$$

$$NO + \left\{\begin{array}{l}K_2S\text{, or}\\ \text{moist Fe, or} \longrightarrow N_2O + N_2.\\ \text{sulphites} \qquad\qquad (NH_3 \text{ also sometimes formed})\end{array}\right.$$

$$\begin{array}{l}NO + HI \longrightarrow NH_3 + I_2.\\ \quad\text{(concentrated solution)}\end{array}$$

$$NO + \text{alk. pyro} \longrightarrow N_2O.$$

$$NO + HNO_3 \text{(sp. gr.} > 1.15) \longrightarrow NO_2 + N_2O_3.$$

$$NO + \text{solution } KMnO_4 \longrightarrow HNO_3.$$

$$NO + O_2 \left\{\begin{array}{l}\text{dry gases} \longrightarrow \text{no reaction.}\\ \text{moisture} \longrightarrow NO_2.\end{array}\right.$$

$$Na_2N_2O_3 + O_2 \text{ (air)} \longrightarrow NaNO_3 + NaNO_2.$$

$$H_2N_2O_3 + KMnO_4 \left\{\begin{array}{l}\text{(acid)} \longrightarrow KNO_3.\\ \text{(alk.)} \longrightarrow KNO_2.\end{array}\right.$$

$$NH_2OH + Cu(OH)_2 \longrightarrow Cu_2O + N_2O \text{ (mainly).}$$

$$NH_2OH + \left\{\begin{array}{l}\text{chromic acid,or}\\ \text{vanadium pentoxide}\end{array}\right. \longrightarrow N_2 \text{ (mainly).}$$

$$NH_2OH + \left\{\begin{array}{l}HgO\text{, or}\\ NaBrO\end{array}\right. \longrightarrow N_2O.$$

$$\underset{\text{(excess)}}{\mathrm{NH_2OH+KMnO_4}}\begin{cases}\text{(strong alk. soln.)}\longrightarrow \text{nitrite}+\mathrm{N_2O}.\\ \text{(weak alk. soln.)}\longrightarrow \mathrm{N_2}+\text{nitrite}+\mathrm{N_2O}.\\ \text{(acid soln.)}\longrightarrow \mathrm{N_2O+HNO_3}.\end{cases}$$

$$\mathrm{NH_4OH}\ \text{(excess)}+\mathrm{Cl_2}\longrightarrow \mathrm{N_2+NH_4Cl}.$$

It is believed that the mechanism given for the reduction of nitric acid aids in the interpretation of these reactions.

Further studies similar to those given in this paper should be made with other reducing agents in order to confirm and amplify the theory offered here, and to determine, if possible, just what the catalyzer is in cases where catalysis plays a part. A study of the action of nitric acid on metals should then follow logically.

Cornell University.

ON ISOTHERMAL REACTION VELOCITY IN HOMO-HETEROGENEOUS SYSTEMS IN THE ABSENCE OF SOLVENT; WITH SPECIAL REFERENCE TO THE CONVERSION OF FUSED MALEIC ACID INTO FUMARIC AND MALIC ACIDS

BY KRISTIAN HÖJENDAHL*

General Theory

The reaction considered under the above heading may be represented by

Liquid ⟶ Solid or Gas.
Gas ⟶ Solid or Liquid.
the latter at constant pressure.

The actual reaction may be uni-or multi-molecular according as one or more molecules of the reactant are involved in it. If the reaction takes place between two (or more) mixed reactants the treatment, which follows, will apply only to those cases in which stoichiometrically equivalent quantities of reactants initially compose the mixture.

For the sake of clearness we shall consider the case of a liquid (fused) reactant, which is giving rise to one or more slightly soluble resultants. Under these conditions we can regard the liquid phase as saturated with the products formed.

Consequently the concentration of these products is constant and equal to the solubilities of the products. During the reaction the concentration remains constant, but the volume of the liquid phase decreases. As the concentration of the reactant is constant its activity must also be constant. Therefore the probability *k*, that a molecule can react in unit of time is constant.

From this it follows, that the total number of molecules which react during time *dt* is

$$-dN = N_t k \, dt$$

where N_t is the number of reactant molecules present at time *t*.

The fraction of the total number of molecules in the system or, what amounts to the same thing, the fraction of originally reactant molecules N_o, which react during unit time is

$$-\frac{1}{N_o}\frac{dN}{dt} = -\frac{d\left(\frac{N}{N_o}\right)}{dt}\left(\frac{N_t}{N_o}\right)k \qquad (1)$$

If the molar fraction $\left(\frac{N_t}{N_o}\right)$ is considered as representing the concentration (volume-concentration has no meaning when applied to the composition of a

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heterogeneous system) the above expression is identical with the usual expression for reaction-velocity for a reaction of the first order. As k is a constant even if the actual reaction is multimolecular it will be seen, that the reaction even then will appear to be of the first order. If more than one compound is simultaneously formed from the same reactant both the probability k_{I} that a molecule of the reactant can form a compound I and the probability k_{II}, that it can form another compound namely II, must be constant.

The fraction of the original reactant molecules, which in time t has formed compound I is

$$-\int_t^o d\left(\frac{N_I}{N_o}\right) = \int_t^o \left(\frac{N_t}{N_o}\right) k_I \, dt = k_I \int_t^o \left(\frac{N_t}{N_o}\right) dt$$

Whilst the fraction which during time t has formed compound II is

$$-\int_t^o d\left(\frac{N_{II}}{N_o}\right) = k_{II} \int_t^o \left(\frac{N_t}{N_o}\right) dt$$

Hence the two compounds are formed in the constant ratio $\left(\frac{k_I}{k_{II}}\right)$

This shows that the Wegscheider test is bound to hold for two simultaneous homo-heterogeneous reactions, whatsoever the actual order of the reactions may be.

The kind of reaction to which the foregoing consideration may be expected to apply may be illustrated by two cases:—

1. The reaction between ethyl-bromide and dimethylaniline (work upon this system is in progress).

2. The decomposition of molten maleic acid. This is considered in the following section.

Conversion of Molten Maleic Acid Into Malic and Fumaric Acids

Maleic acid melts at 130-131° and decomposes above that temperature with measurable velocity to form several products among which fumaric acid is the predominant one. Fumaric acid is precipitated during the reaction. According to Skraup[1] i-malic acid and maleic anhydride are formed as well.

Tanatar[2] confirms the main results of Skraup.

Skraup finds, that maleic anhydride is formed in greater amount than would be expected from the equation:

$$2 \text{ maleic acid} \longrightarrow \text{maleic anhydride} + \text{malic acid}$$

Skraup determines maleic anhydride as the part dissolved in some benzene present in the heating tube. Probably the presence of benzene has affected the process. In the light of subsequent results obtained by the writer, it would appear that maleic anhydride is formed to a minute extent by the following reaction.

$$\text{maleic acid} \rightleftarrows \text{maleic anhydride} + \text{water}$$

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[1] Monatsheft, 12, 107 (1891); 14, 501 (1893).

[2] Ber. 27, 1365 (1894).

This equilibrium is disturbed if maleic anhydride is removed by benzene. The water formed simultaneously can furthermore cause the following reaction:

maleic acid + water ⟶ malic acid

wherefore also malic acid is formed in greater amount if benzene is present. This probably accounts for the curious results of Skraup. By heating with benzene for 2 hours at 120° he obtains 32% anhydride and 10% malic acid, while by heating without benzene for 9 hours at 130° he only obtains 12% malic acid.

Weiss and Downs[1] have investigated mainly the transformations of fumaric acid and maleic acids in aqueous solutions.

Warburg[2] has investigated the photochemical change:

$$\text{fumaric acid} \rightleftarrows \text{maleic acid.}$$

He finds that fumaric acid attacks glass, a phenomenon the writer has also observed.

Application of the Theory of Homo-Heterogeneous Reaction Velocity

The following four reactions probably take place in molten maleic acid:

(I). maleic acid ⟶ fumaric acid

(II). 2 molecules maleic acid ⟶ malic acid + maleic anhydride.

(III). maleic acid ⇄ maleic anhydride + water

(IV). maleic acid + water ⟶ malic acid

The equilibrium for (III) is so much in favour of maleic acid, that this reaction and (IV), which depends upon it may be neglected at present.

If *k* in equation (1) is not taken to be a constant then (1) is a general equation for any reaction. In this case we therefore can write the velocity of reaction (II) above thus

$$\text{vel}_2 = -\frac{1}{N_0}\frac{dN}{dt} = \frac{N_t}{N_0} \times k_2$$

Let N_{ft}, N_{at} and N_{ht} denote the number of molecules of fumaric acid, malic acid and maleic anhydride respectively, which during time *t* are formed from N_0 molecules of original maleic acid. Then:

$$N_t = N_0 - N_{ft} - N_{at} - N_{ht}$$

N_t varies rapidly, due to the formation of fumaric acid by reaction (I), which is a swift reaction.

k_2 depends on the concentration of maleic acid in the liquid phase, This does not contain fumaric acid but all the other components. The molar fraction of maleic acid at time *t* with respect to the liquid phase only therefore is:

$$\frac{N_t}{N_t + N_{at} + N_{ht}}$$

N_{at} and N_{ht} are formed by the slow reaction (II) therefore N_{at} and N_{ht} are small compared with N_t and also with the decrease in N_t. The molar

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[1] J. Am. Chem. Soc. 44, 1118 (1922).

[2] Sitzungsber. preuss. Akad. Wiss. 50, 964 (1919).

fraction therefore will remain nearly unity and k_2 will with approximation be a constant. This means that reaction (II) as well as reaction (I) approximately will be of the first order.

For the same reason the Wegscheider test will hold for the same two reactions.

Analytical Methods

As to the analytical methods all previous investigations have determined fumaric acid as that part, which does not dissolve in water, allowance being made in some cases for the solubility of the acid in water.

For the determination of malic and maleic acids several methods have been developed, but the authors themselves state that these methods are not very satisfactory. Therefore a method has been developed depending mainly on electrical conductivity and titration of total acid. Briefly the method consists in taking the melt (0.05 gram molecule) dissolving it in so far as it will dissolve in 25 cc of water at 25°. This takes several days. It is then filtered, the filtrate diluted with conductivity water to 1 or 1/2 litre and conductivity and titration-measurements carried out on this, the malic part, of the analysis. A certain amount of fumaric acid is dissolved in this part which amount is obtained from solubility data.

The undissolved residue consisting mainly of fumaric acid is then dissolved in hot water and diluted to 1 or 1/2 litre. This is sufficient to keep the fumaric acid dissolved when cooled. On this part of the analytic mixture, which is termed the fumaric part the titer and the specific conductivity are determined in a manner quite similar to that employed in the malic part of the analytical mixture.

The experimental values for specific conductivity and total acid are then employed in the formulae deduced in the following.

The Specific Conductivity of Mixed Aqueous Solutions of Inactive Malic, Maleic and Fumaric Acids

Arrhenius[1] has considered the ionisation of mixed electrolytes and outlined the theory of isohydric solutions. F. Barmwater[2] has calculated the conductivity of mixed solutions of two weak acids on the basis of the mass-action equation. He arrives at a third order equation.

In the treatment given below equations of the third order are to a large extent avoided. The terms occurring in the various equations employed are as follows:—

σ = the specific conductivity of the solution.

$K = \frac{1000}{\mu_\infty}$ = a constant experimentally determined to be 2.575

c_a, c_m and c_f denote the concentrations (moles per litre) of malic, maleic and fumaric acid respectively.

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[1] Z. physik. Chem. 2, 284 (1888).

[2] Ibid. 45, 557 (1903).

$k_a = 3.99 \times 10^{-4}$; $k_m = 1.34 \times 10^{-2}$ and $k_f = 9 \times 10^{-4}$ denote the first stage dissociation-constant for the acids.

γ_a, γ_m and γ_f denote the degrees of dissociation of the three acids respectively in the mixture.

τ = the total acid (moles per litre) determined by titration.

To render the treatment feasible it is necessary to make certain reasonable assumptions. In the first place the conductivity has to be determined at concentrations, at which the gas laws hold. In the second place the second stage of dissociation has been neglected as being very small compared with the first. In the third place the mobilities of the three acid anions have been assumed to be equal. This of course only holds because of the very similar size and constitution of the acid anions. In consequence of this the specific conductivity of the mixture may be put proportional to the concentration of hydrogen ions. The proportionality constant is K. Therefore

$$\sigma K = c_a\gamma_a + c_m\gamma_m + c_f\gamma_f. \qquad (1)$$

Applying the law of mass-action to the dissociation we get:

$$\frac{c_a\gamma_a(c_a\gamma_a + c_m\gamma_m + c_f\gamma_f)}{c_a(1-\gamma_a)} = k_a \qquad (2)$$

and similarly for the other two acids.
Substituting σK for the concentration of hydrogen ions:

$$\frac{\gamma_a \sigma K}{1-\gamma_a} = k_a$$

or

$$\gamma_a = \frac{k_a}{\sigma K + k_a} \text{ and two similar equations.}$$

Substituting these values of γ_a, γ_m and γ_f in equation (1) we obtain:

$$\sigma K = \frac{c_a k_a}{\sigma K + k_a} + \frac{c_m k_m}{\sigma K + k_m} + \frac{c_f k_f}{\sigma K + k_f} \qquad (3)$$

$$\sigma K = \sqrt{\frac{c_a k_a}{1 + \frac{k_a}{\sigma K}} + \frac{c_m k_m}{1 + \frac{k_m}{\sigma K}} + \frac{c_f k_f}{1 + \frac{k_f}{\sigma K}}} \qquad (4)$$

One more equation is needed. This is obtained by titrating the solution:

$$\tau = c_a + c_m + c_f$$

Whence:

$$c_m = \tau - c_f - c_a \qquad (5)$$

Inserting this in equation (3) we obtain:

$$\sigma K = \frac{c_a\ k_a}{\sigma K + k_a} + \frac{(\tau - c_f)\ k_m}{\sigma K + k_m} - \frac{c_a k_m}{\sigma K + k_m} + \frac{c_f k_f}{\sigma K + k_f}$$

From this the following formula for the determination of the concentration of malic acid in the mixture is obtained:

$$c_a = \frac{\dfrac{(\tau - c_f)k_m}{\sigma K + k_m} + \dfrac{c_f\ k_f}{\sigma K + k_f} - \sigma K}{\dfrac{k_m}{\sigma K + k_m} - \dfrac{k_a}{\sigma K + k_a}} \qquad (6)$$

As mentioned earlier c_f is known from solubility measurements. c_m is then calculated from (5).

The expression to be used for the fumaric part of the analysis is obtained from the above by changing the suffixes and neglecting the very small magnitudes containing c_a

It is:

$$c_m = \frac{\sigma K - \dfrac{\tau\ k_f}{\sigma K + k_f}}{\dfrac{k_m}{\sigma K + k_m} - \dfrac{k_f}{\sigma K + k_f}} \qquad (7)$$

To verify the formula deduced, conductivity measurements of mixed aqueous solutions of maleic, malic and fumaric acid were carried out. The ordinary Wheatstone-bridge method with telephone was employed. The results are given in the following two tables. The temperature is 25°±0.1

c_m	c_a	Experimental conductivity	Calculated conductivity
0.0495	0.0000	0.007746	0.007750
0.0445	0.0049	0.007293	0.007270
0.0396	0.0099	0.006850	0.006785
0.0347	0.0148	0.006310	0.006272
0.0297	0.0198	0.005740	0.005730
0.0248	0.0247	0.005150	0.005140
0.0198	0.0296	0.004550	0.004515
0.0148	0.0345	0.003880	0.003840
0.0099	0.0395	0.003123	0.003105
0.0050	0.0444	0.002373	0.002377
0.0000	0.0493	0.001630	0.001645

c_f	c_m	c_a	Experimental conductivity	Calculated conductivity
0.005	0.045	0.000	0.007266	0.007265
0.005	0.035	0.010	0.006247	0.006293
0.005	0.025	0.020	0.005094	0.005178
0.005	0.015	0.030	0.003843	0.003900
0.005	0.010	0.035	0.003143	0.003198
0.005	0.005	0.040	0.002439	0.002459
0.005	0.000	0.045	0.001746	0.001748

That the experimental conductivities in the latter table are rather low is probably due to the attack of fumaric acid on glass as observed by Warburg.

The Reaction-Velocity Measurements

The materials employed were kindly presented by Messrs. Weiss and Downs.

The maleic acid was purified by recrystallisation from acetone solution.

The investigations were carried out in a gas heated and electrically regulated thermostat containing liquid paraffin. The bulb of the thermoregulator was filled with air and the temperature was kept to 0.5°. The thermometer used was specially made and was calibrated by the National Physical Laboratory (England) to 0.1°

Owing to the effect of fumaric acid on glass as stated previously the vessels containing the reacting mixture were test tubes of fused quartz. The walls of these were very bad heat conductors. Hence the charge (5.8 grams maleic acid + 1 gram fumaric acid) was fused over a bunsen-burner, whereupon the tube was immersed in the thermostat and left there for a given time, after which the tube was taken out and the contents cooled suddenly by adding 25 cc of water.

The mode of analysis has already been described.

The results of the measurements are collected in the following tables and diagrams.

TABLE I

Temperature 139.6°C.

time sec	fumaric acid	malic acid	maleic anhydride	maleic acid	k_{uni} fumaric	k_{uni} malic	k_{bi} malic	Wegscheider test
546	0.052	0.008	0.008	0.932	7.5×10^{-6}	1.5×10^{-6}	1.6×10^{-6}	6.5
3270	0.213	0.042	0.042	0.703	6.98	1.54	2.2	5.07
6980	0.368	0.080	0.080	0.472	6.91	1.50	3.2	4.60
12420	0.511	0.105	0.105	0.279	7.2	1.40	5.0	4.77
			average		7.2×10^{-6}	1.50×10^{-6}		4.85

TABLE II

Temperature 149.8°C.

time sec	fumaric acid	malic acid	maleic anhydride	maleic acid	k_{uni} fumaric	k_{uni} malic	k_{bi} malic	Wegscheider test
990	0.138	0.033	0.033	0.796	11.4×10^{-6}	3.4×10^{-6}	4.8×10^{-6}	4.2
3480	0.312	0.082	0.082	0.523	10.9	3.3	6.4	3.78
7200	0.490	0.131	0.131	0.248	12.5	3.1	11.9	3.75
14190	0.657	0.153	0.153	0.038				4.3
				average	11.4×10^{-6}	3.3×10^{-6}		4.0

The values for maleic anhydride are calculated on the assumption that malic acid and maleic anhydride are formed in equal amounts according to the equation

2 molecules maleic acid ⟶ malic acid + maleic anhydride.

Reaction velocity data were likewise obtained in glass vessels. They are not as exact as those quoted and are consequently omitted here.

Discussion of Results

It will be seen, that the measurements give results, which are in close agreement with the theory.

Especially the curves for malic acid are unimolecular with an exactness equal to the experimental error. It is surprising that the fumaric acid especially in the latter table shows a deviation from the unimolecular scheme, which is definitely outside the experimental error. This deviation may be due to the reaction:

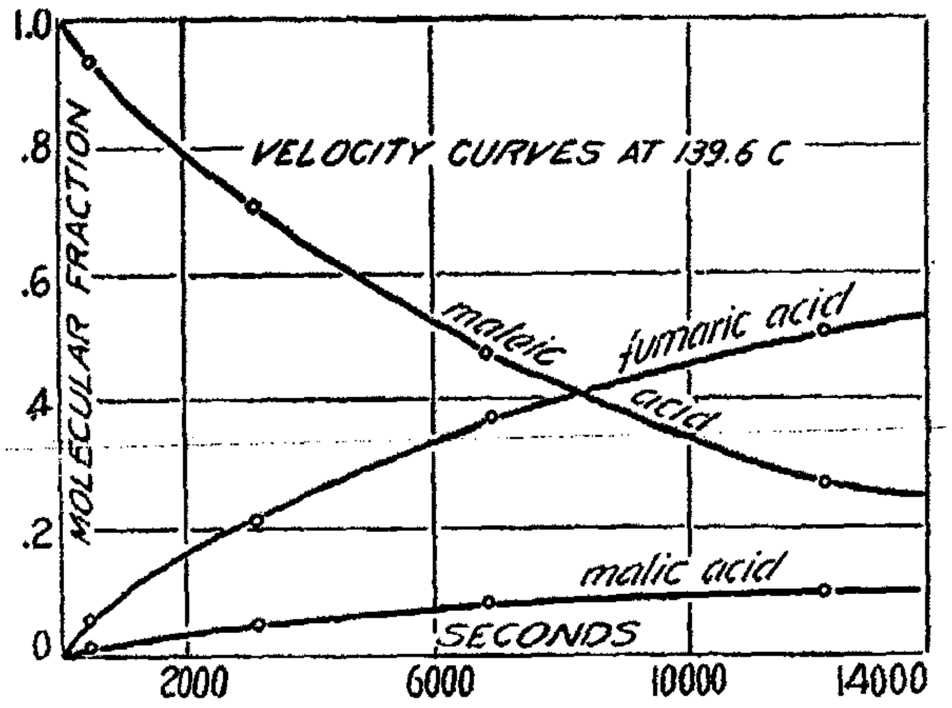

Diagram 1.

Maleic acid $\rightleftarrows$ maleic anhydride + water

the equilibrium for which at the lower temperature 140° is entirely in favour of maleic acid, as shown by the applicability of the preceding theory. At 150° it may be shifted sensibly from left to right in the earlier stages of the run. Later on this reaction will go back again partly because of the disappearing

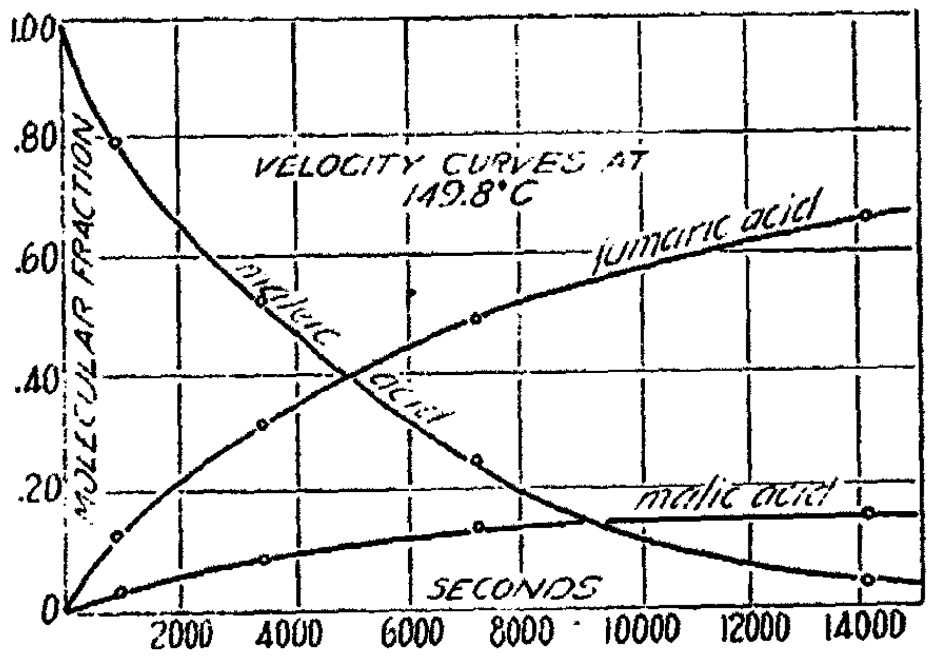

Diagram 2.

maleic acid and partly because of the maleic anhydride formed by the reaction:

2 moles maleic acid ⟶ malic acid + maleic anhydride

At 140° the dissociation of maleic acid into anhydride and water is considerably smaller although appreciable. The velocity-constant for fumaric acid therefore is a better constant.

At 160° on the other hand the dissociation is so prominent that the vapour pressure of water + anhydride is equal to 1 atmosphere. At this temperature maleic acid boils with decomposition to water and maleic-anhydride vapour.

The Infra-Red Absorption Band

The critical increment or energy of activation of the reaction:

maleic acid ⟶ fumaric acid

can be determined by help of the Marcelin-Rice equation:

$$\frac{d \log_e k_{uni}}{dT} = \frac{E}{RT^2}$$

Inserting the average values of k_{uni} for fumaric acid from the tables the following value is obtained:

$$E = 15800 \text{ cal}$$

From this the position of the infra-red absorption-band[1] is calculated using the equation:

$$E = h\nu$$

A wave length of $\lambda = 1.80\mu$ is obtained.

This has been verified experimentally using a Hilger infra-red spectrometer and a radiomicrometer[2]. As source of radiation a Nernst glower was used.

A cell containing fused maleic acid was obtained in the following manner. Fused maleic acid was placed between two heated sheets of quartz and allowed to cool. The sheets were then placed between the Nernst glower and the spectrometer. After some time the central part of the film of solid maleic acid melted. By regulation of the current through the Nernst glower it was arranged, that the central part was kept just molten. The edges of the film were kept solid by screening the radiation, the solid maleic acid thus formed a part of the cell. As solid fumaric acid was formed in the melt no attempt was made to obtain any extinction-coefficient. The result is shown in the appended diagram (3), which shows the deflections observed in the case of three samples of maleic acid. The fourth curve shows the deflection observed for the case of the Nernst glower itself. In this case the width of the slits has been reduced so that the observed deflections might be comparable with the other readings. Curve IV gives the shape which the deflection curves would possess, if no selective absorption were present. Such curves are represented by dotted

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[1] Lewis: J. Chem. Soc. 109, 796 (1916).

[2] See Taylor and Lewis: J. Chem. Soc. 121, 665 (1922).

lines. The divergences represent the selective absorption. The observed bandheads viz. 1.80, 1.85 and 1.75μ are in good agreement with the calculated value 1.80μ. No other band was observed in the region 0.8 to 3.5μ Beyond 3.5μ there seem to be more bands, but the deflections for this region were too small to give any trustworthy values.

In connection with this work it was observed, that maleic acid is dimorphous. The crystalline film formed by the solidifying of the fused maleic acid changes after a short time into a white aggregate of crystals.

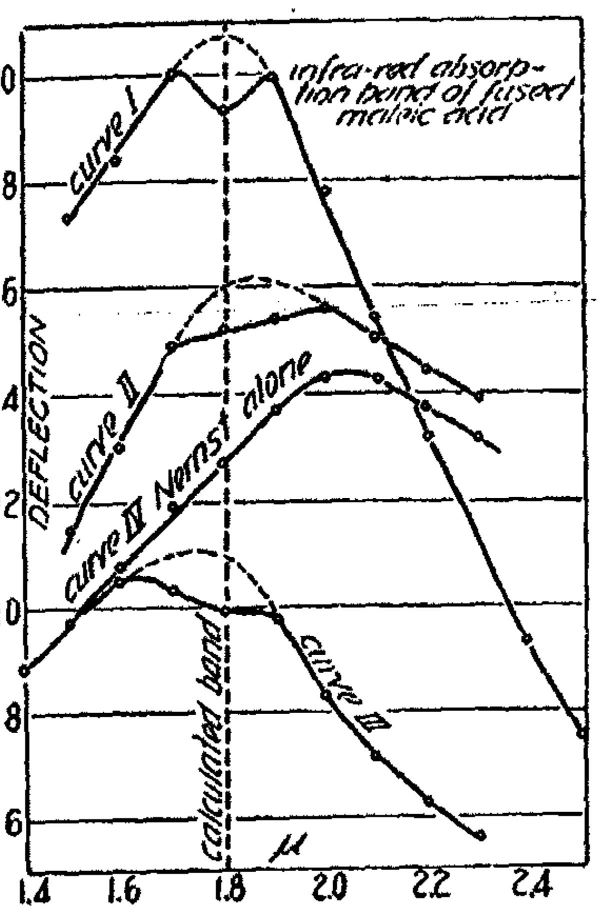

Diagram 3.

Dimorphous maleic acid has been observed crystallized from different solvents by Biilmann and Lund.

On the Absolute Value of the Velocity-Constant of the Transformation of Maleic to Fumaric Acid

It is of interest to compare the observed unimolecular velocity-constant of the formation of fumaric acid from fused maleic acid with that calculated on the basis of the radiation hypothesis of thermal change and also with the empirical equation of Dushman, the latter being known to agree satisfactorily with the unimolecular (but catalysed) velocities for the decomposition of gaseous phosphine and gaseous nitrogen-pentoxide respectively.

As pointed out by W. C. M. Lewis[1] on the assumption that the rate of absorption of energy by a Planck oscillator is continuous it follows that the unimolecular velocity-constant should be given by:

$$k_{uni} = 2.465 \times 10^{-22} n^3 \nu^2{}_e^{\frac{-E}{RT}}$$

Dushman's equation is:

$$k_{uni} = \nu_{o}{}^{\frac{-E}{RT}}$$

In the case now under consideration the experimental values of E and ν are:

E = 15800 cal; $\nu = 1.667 \times 10^{14}$ per sec.

Dushman's equation gives:

$k_{uni} = 7.8 \times 10^{6}$

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[1] Phil. Mag. 39, 26 (1920).

Lewis' equation gives for n = 1:
$k_{uni} = 3.2 \times 10^{-2}$
whilst the experimental value is:
$k_{uni} = 7.2 \times 10^{-5}$

The observed velocity-constant lies nearer the equation of Lewis than that of Dushman, but there is no quantitative agreement. It is the first known case in which the observed velocity constant is less than that given with the radiation-hypothesis using Planck's oscillator.

It is to be concluded apparently that the rate of decomposition is much less than the rate at which active molecules are formed, i.e. the majority of the active molecules become de-activated instead of decomposing. It is possible that in a homogeneous liquid state we are here dealing with a case in which collisions are significant for deactivation.

Summary

(1). An expression for the reaction-velocity in homo-heterogeneous systems has been outlined. The expression arrived at shows that the process will apparently be of the first order even if the actual reaction is multimolecular. Hence the Wegscheider test necessarily holds for two simultaneous homo-heterogeneous reactions. Catalysis generally will give a deviation from the first order.

(2). An expression for the electrical conductivity of aqueous mixed solutions of maleic malic and fumaric acids has been deduced and tested experimentally. An analytical method based on electrical conductivity-measurements and titration of acid has been developed for the analysis of a mixture of maleic, malic and fumaric acids.

(3). The rate of formation of fumaric and malic acid respectively formed from maleic acid in the molten state has been determined experimentally at the temperatures 140°C. and 150°C. In accordance with the theory outlined above both of the reactions:

$$\text{maleic acid} \longrightarrow \text{fumaric acid}$$

and

$$2 \text{ molecules maleic acid} \longrightarrow \text{malic acid} + \text{maleic anhydride}$$

are found to be of the first order.

(4). For the case of the reaction

$$\text{maleic acid} \longrightarrow \text{fumaric acid}$$

the critical increment and the position of the infra-red band have been calculated. The latter has been determined experimentally. A good agreement with the calculated value is obtained.

(5). The observed velocity constants have been compared with certain theoretical expressions.

The author wishes to express his thanks to the Ramsay Memorial Fellowship Trust and the Danish Committee for the award of a grant.

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NITROCELLULOSE AND CAMPHOR

BY J. B. NICHOLS

As part of my senior research in the autumn of 1922 I was asked by Professor Bancroft to determine, if possible, whether camphor peptized or dissolved the nitrocellulose known as pyroxyline. If the pyroxylin went into true solution, we could determine its molecular weight. If it did not, we had made a definite advance towards the theory of the formation of celluloid.

The method employed consisted in determining whether small additions of nitrocellulose did or did not lower the freezing-point of camphor. A Beckmann thermometer was set for a range from 170° to 176°. The camphor was placed in a freezing-point tube equipped with the thermometer and a copper stirring rod; this tube was surrounded by a larger tube which gave air insulation from the bath of Crisco. As the result of several determinations, the melting-point of camphor was found to be 172.1° or 175.5° when corrected for the error due to the emergent stem. The camphor did not have a sharp melting-point, however, and became slightly brownish after several heatings and coolings. This might be due either to pieces of cork falling into the camphor or to the copper stirring-rod, so both sources of error were eliminated. A glass stirring-rod was substituted for the copper one and the hole through the cork was protected by a short piece of glass tubing. Camphor sublimes so readily that it was found necessary to bring the level of the bath as near as possible to the top of the tube. These changes eliminated the brownish discoloration.

When pyroxylin was added, it apparently went into solution and the freezing-point was lowered 6°-8°. A quantity of bubbles was given off, however, indicating the probable decomposition of the cellulose in molten camphor at 180°. The mixture solidified to a reddish-brown mass and had a sickening odor similar to that of acrolein. Another sample of camphor was melted and pyroxylin added; but the gas evolved was collected in a gas-sampling tube, the first 100 cc being discarded as chiefly air swept out of the freezing-point tube. The next 100 cc of gas were analyzed and were found to consist of carbon dioxide, carbon monoxide, nitric oxide, and nitrogen with no hydrocarbons and no hydrogen. This analysis agrees with that made by Pfyl and Rasenack[1] of the gases given off during the slow decomposition of nitrocellulose. It seems therefore safe to conclude that the gases come from the decomposition of the nitrocellulose and not from the camphor.

If some substance could be added to the camphor which would lower its melting-point, it might prove possible to add nitrocellulose without decomposition, though that introduces the peculiarities of ternary mixtures. Monobrom-camphor seemed the best choice because it melts at 76° and does not

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[1] Chem Zentr. (5) 13 II, 763 (1909).

boil until 274°. A preliminary run showed that pyroxylin has no effect on the melting-point of monobromcamphor. Since some pyroxylin seemed to dissolve, this showed that monobromcamphor peptizes nitrocellulose to some extent; but when more than two percent of nitrocellulose was added, the monobromcamphor peptized it with difficulty.

The freezing-point curve for mixtures of camphor and monobromcamphor was then determined and the eutectic was found to occur at 62.3° with a composition of 15% camphor and 85% monobromcamphor. The data for the curve are given in Table I.

TABLE I

% Bromcamphor	F.Pt. (corr.)	% Bromcamphor	F.Pt. (corr.)
0.	175.4°	83.3	84.0°
16.7	157.0	84.0	63.15
28.6	142.4	84.7	62.5
40.0	127.3	85.5	62.3
48.2	114.9	87.0	63.7
62.5	91.8	90.9	67.0
71.4	77.85	100.0	74.8

Since the volatilization of camphor from a mixture with monobromcamphor would change the composition and the freezing-point, it was not safe to go above 100° and a water-bath was therefore substituted for the Crisco bath. To a mixture of 20 grams of monobromcamphor and 5.8 grams camphor, having a freezing-point of 71.2° there were added 0.2 grams of pyroxylin. A careful determination of the freezing-point gave a value of 70.8° or a lowering of 0.4°. Addition of 0.2 grams pyroxylin lowered the freezing-point another 0.4°, to 70.4°. Another run was made, using a different mixture freezing at about 90°, and approximately the same results were obtaind. These data seemed to indicate that pyroxylin dissolves in melted camphor. Using 49800 as the cryoscopic constant for camphor, the molecular weight of the nitrocellulose came out about 4300, indicating a formula with n = 16.

It was possible, however, that this lowering of the freezing-point might be due to moisture adsorbed by the nitrocellulose and it was calculated that this lowering of the freezing-point might be obtained if the pyroxylin contained 0.5% water. A couple of drops of water were added to a mixture of camphor and monobromcamphor freezing at 91.9°, and the freezing-point was lowered nearly two degrees.

A one-gram sample of pyroxylin was therefore dried for a day in a vacuum desiccator over sulphuric acid and was then reweighed. It was found to have lost the 0.005 grams of water which was supposed to be present. To a mixture of 15 grams monobromcamphor and 6 grams camphor freezing at 78.4°, there were added 0.2 grams of thoroughly dried nitrocellulose. No lowering of the freezing-point could be detected and a further addition of 0.2 grams had also no effect. In order to check this, 0.2 grams of dried pyroxylin were added to another mixture freezing at 91.1° and no change of freezing-point could be detected.

This proved conclusively that no true solution is formed and that camphor peptizes nitrocellulose. With the specially-dried pyroxylin, peptization took place almost immediately, while peptization was relatively slow with the pyroxylin containing traces of moisture. The addition of more than 7-8% pyroxylin (referred to camphor) rendered the mixture so viscous that no definite freezing-point could be determined.

The general results of this work are:—

1. Pyroxylin decomposes when added to melted camphor, yielding carbon dioxide, carbon monoxide, nitrogen, and acrolein.

2. Monobromcamphor peptizes pyroxylin slightly.

3. The camphor-monobromcamphor freezing-point curve has been determined. The eutectic temperature is 62.3° and the eutectic composition 85% monobromcamphor.

4. Small amounts of moisture in nitrocellulose decrease the rate of peptization by camphor.

5. Nitrocellulose does not lower the freezing-point of camphor. Camphor, therefore, peptizes pyroxylin and does not carry it into true solution.

Cornell University.

NEW BOOKS

Colloid Chemistry. *By The Svedberg. 23 × 16 cm; pp. 265. New York: The Chemical Catalog Company, 1924. Price: $3.00.* This monograph is based on a series of lectures given at the University of Wisconsin during the spring and summer of 1923. The general treatment deals with the formation of the colloid particle, the colloid particle as a molecular kinetic unit, and the colloid particle as a micell. There should be a fourth part on the destruction of the particle; but that cannot be written at present owing to lack of data.

"The science of colloids is, as a rule, dealt with as a part of physical chemistry. This assumption may be all right and to a considerable extent founded in the nature of the colloid phenomena but, admitting this, we should bear in mind that the principle used in collecting the colloid phenomena and arranging them to a science is not the same as the principle used in putting together or discerning the ordinary branches of physics and chemistry. Colloid chemistry, for instance, is not like electro-chemistry, photo-chemistry, thermo-chemistry, electricity, etc., the science of a certain group of phenomena, *it is the science of a certain group of material systems,* the science of systems of a certain structure. In this respect, colloid chemistry resembles to a certain extent, bio-chemistry. Bio-chemistry is the science of certain systems—not so much certain phenomena," p. 11.

"Research in colloid chemistry is at present working along two different lines: (1) the study of artificial systems of greatest possible simplicity with the object to find out general laws; (2) the study of natural systems which appear in the organisms or as technical products of high importance, with the object to learn their properties and the way to their synthesis. These two branches of research ought to support one another, the former can give directive rules for the latter; the latter offers suggestions and occasionally pure-cultivated systems to the former branch. The systems which the latter branch is treating are as a rule rather complicated; and, frequently rather ill-defined. We may ask if it would not be more rational to confine research to an intense study of the former class of systems—the more simple colloids,—and leave the second class for the present. The answer is, that the systems of the second class are of such overwhelming importance that every little progress *today* is of the greatest value—we cannot afford to wait for the general results which no doubt the former branch will give us, we must see what can be gained *now*. On the other hand I think it might be worth while to bear in mind that in the long run the simpler systems will be of considerable importance for the study of the systems of the latter class; nay—it might be the only way to get results of a more permanent value."

Svedberg's point of view is not quite that of some of us, p. 12. "The chief problem of Colloid Chemistry is the investigation of the structure of colloid systems. The astonishingly rapid growth of this science may be attributed to the fact that both Chemistry and Physics have for a long time been developed without regarding the influence of ultramicroscopic structure on a great many phenomena. Now we know that the main part of all living beings is built up of colloids, of systems possessing a specific structure; and, that a number of very important technical products derived from organisms are colloids—hence the great interest which the bio-sciences or the medical sciences and industry take in colloid chemistry. So, for instance, to name some technical applications, colloid chemistry is of importance in the industries of tanning, dyeing, fermentation, cellulose products, starch, gelatin, glues, soaps, rubber, nitrocellulose, celluloid, textile products, dairy, agriculture, bread-making, asphalt, petroleum, photography, clay products, cements, in the purification of water, etc.

"The important thing in colloid chemistry is not to measure all possible properties of the colloid system; it is to find out its structure in a wider sense of the word—for this knowledge will enable us to arrange the colloid systems within the general frame of chemistry and physics. It is because we do not know the structure of the colloid that we are forced to make a special science of them."

On p. 17 is the clearest statement that the reviewer has yet seen of what the physicists mean by molecular weight. "The theory of the Brownian movements was worked out by Einstein in 1905 upon the assumption that it is due to the impacts of the surrounding molecules and that the translatory kinetic energy of a suspended particle is equal to the energy of a molecule. We have been able to check up this theory and we have found that the particles behave indeed as if they were heavy molecules—the molecular weight corresponding to the apparent weight of the particle." There are really two definitions here though they are apparently interchangeable and therefore interdependent. The molecular weight of a substance is the weight of the mass of that substance which has the same translatory kinetic energy as two grams of hydrogen gas at the same temperature. The apparent weight of a suspended particle is its molecular weight. Neither of these definitions—if there are two—will be acceptable to the chemist and it is a pity to use any scientific term in two quite distinct terms. Soddy claims that the chemists should abandon their usage because the definition of the physicists is less vague. One might ask whether the definition of the physicists has yet proved its value.

On p. 59 the author seems to have made trouble for himself unnecessarily. "Besides the nuclear method, there is another very curious way of varying the degree of dispersity when making a gold colloid, namely, by exposing the reduction mixture to ultraviolet light during the reduction. Nordenson, working in the laboratory of the writer, found the following phenomenon. If you take a dilute gold chloride solution and add hydrogen peroxide, the reduction proceeds very slowly—will take perhaps one-half hour and we get a very coarse colloid. Now if we expose the reduction mixture to ultraviolet light, the velocity of reduction increases very rapidly and we get a fine-grained colloid. The length of exposure determines the degree of dispersion. An exposure of 25 sec. to the light of a strong mercury quartz vapor lamp reduces the size of the particles from say 100 $\mu\mu$ — the size we get without illumination—to 10 $\mu\mu$.

"A satisfactory explanation of this peculiar process has not yet been found. It is evident that the number of nuclei is increased by the action of the ultraviolet light, but the mechanism of this action is quite unknown. The light itself has a slight reducing action, *i.e.* if no hydrogen peroxide is added, we still get a sol,—but a very coarse one, and it takes a considerable time to get the gold chloride reduced."

To the reviewer it seems that hydrogen peroxide acts as a depolarizer, increasing the efficiency of the light. The reaction can then be written:

$$2\,AuCl_3+3H_2O_2=2\,Au+6\,HCl+3O_2.$$

There is a very interesting discussion of the photographic emulsion, pp. 68-78. "The most important of dissociation processes is, of course, the dissociation of the silver halides. Lorenz found that if we expose an optically empty crystal of silver bromide to light, there are produced particles that can be seen in the ultramicroscope and they, no doubt, consist of metallic silver. If we expose halides to a very feeble illumination no particles can be seen but upon treating the halide with a developer, *i.e.* a reducing agent of proper reducing potential, reduction to metallic silver takes place. Probably there are present very small silver particles in such feebly exposed halide crystals—particles too small to be seen in the ultramicroscope. The photographic process is very likely based on the formation of such very small silver particles in or on the surface of the silver halide grains in the film, and the writer, therefore, thinks he is justified in giving a short report on the recent advances in the study of the photographic processes under the heading of formation of disperse systems by dissociation. . . .

"A statistical study of the percentage number of grains remaining unchanged after development in contact with developed grains has given the result that there is no affecting of a grain by the reduction process in another grain close to it. According to experiments in the Eastman Kodak Laboratory, there is, however, such a transfer in cases where the crystals are in actual molecular contact with each other, *i.e.* where the grains have actually become part of one and the same crystal building. If there is a thin layer of gelatin between the particles, there is no development of one grain by the other.

"We have also measured the diameter of the grains left after developing and dissolving away of silver and compared this value with the diameter of the same grains before development. It was found that the diameter of those grains is not changed even if they are close to a grain that has been reduced. It, therefore, seems that at least in certain cases the halide grain is the unit in the photographic process. It is either developed as a whole or not developed at all.

"There are, however, cases where a complete reduction of the grains does not take place. If we add very much potassium bromide to our developers, and study the grains before and after developing and after removing the silver, some of the remaining grains have become irregular in shape showing that part of them has been developed and then dissolved. This is rather important for practical photographic work, for the structure of the silver in the negative depends on whether the whole halide grain has been reduced or not. If it is reduced only partly, we get another kind of graininess in the negative. So for certain processes it is better to use a developer that does not reduce the whole grain but just part of it. From this practical point of view, it is important to study the conditions for complete and incomplete development. . . .

"If we sum up the results arrived at by using these new methods for studying photographic processes, we have the following facts. The halide grain is the unit of the photographic process. At least under certain conditions, it is made either completely developable or not developable—we have simply to measure the percentage number of developable grains. For α-rays and β-rays we probably have the same kind of curve—the exponential line. In the case of α-rays, the exponent is actually equal to the number of α-rays striking the grain; in the case of β-rays, the number is smaller. It has been possible to make the starting points of development visible. Those points or developable centers are comparatively few in number and they increase with exposure. At least one center is necessary to make a grain developable and accordingly the percentage number of developable grains for a certain exposure is given by the formula

$$P = (100 - e^{-v}).$$

We can calculate the average number of centers from the number of developable grains. If we trace the curve showing the relation between exposure and number of centers per unit area of grain, we get for the α- and β-rays a straight line, and for light a curve that at first is convex and then goes over into a straight line. For α- and probably β-rays, this number means the number of α- respectively β-particles absorbed per unit area of the surface of the grain and is probably the same even for different emulsions. In the case of light, however, we get different curves for different emulsions."

"It seems to me that all the facts so far known may be explained on the basis of the following hypothesis. The surface of the halide grain is capable of supplying the material for the formation of a developable center in all its points, but the sensitivity—defined as the least amount of energy required to make a certain spot reducible by a developer of a certain reduction potential—varies from point to point considerably. The variation in sensitivity is probably due to the action of the gelatin and other substances added to the emulsion, and to the way of making the emulsion.

"The energy of the α-particles is high enough to produce a developable center—probably an ultramicroscopic silver particle big enough to act as a condensation center—wherever it strikes the grain. We accordingly get the exponential curve and the number kt in the formula

$$P = 100(1 - e^{-kt})$$

is equal to the number of α-particles striking the grain. The energy of a β-particle or of a high-frequency quantum (short-waved X-rays) is still high enough to produce a developable center; but every β-particle and every X-ray quantum striking the halide grain does not give off energy enough in the surface layer of the grain. We therefore get an exponential curve obeying the above equation, but kt is less than the number of β-particles or of quanta striking the grain, or even absorbed in the grain. It is also possible that not all the spots of the halide grain surface are sensitive enough to β-particles or X-ray quanta. The energy of a quantum of ordinary light is too small to give a developable center. It is necessary that a certain minimum number of light quanta are absorbed within a certain maximum area of the grain surface to produce a developable center. Hence we get a curve with an inflexion point, and a big number of quanta must be absorbed per grain to make a developable center.

"This assumption would involve the hypothesis that those centers or starting points would probably consist of a little nucleus of silver, a tiny colloid silver particle, and that it is necessary that this silver particle reach a certain minimum of size before it can act as a condensation nucleus in the process, just as Zsigmondy has found that the gold particles must reach a certain size to act as nuclei in the gold reduction process."

We are of course interested in Svedberg's views on adsorption, pp. 167-178. "If we try to define adsorption it is obvious that in the extreme, adsorption is very different from chemical reaction, but also that there are cases where the difference is not so marked. A very striking feature is that adsorption often takes place in cases where we hardly would expect any chemical reaction—*e.g.* the adsorption of the noble gases by charcoal and the adsorption of different inactive substances by the noble metals, platinum, etc. Even in cases where we have never found any chemical compounds—*e.g.* in helium and argon—there is a very marked adsorption. The volume of argon adsorbed by one gram of cocoanut charcoal at 9° C. is 12 cc., with hydrogen only 4 cc., and with nitrogen 15 cc.

"This shows that the forces involved in the adsorption phenomena are, as a rule, rather different from the forces in ordinary chemical compounds. We have never been able to isolate a chemical compound containing argon, yet we have in it such a marked adsorption.

"If we try to imagine the forces involved, we might assume that at the boundary surface part of the valences binding the atoms together are free in the form of secondary or partial valences and that they are responsible for adsorption. That would make possible a certain distinction between chemical compounds and adsorption compounds, the former being built up chiefly by means of primary valences. Naturally, in the future when we are able to calculate the force between the electrons and the positive nuclei in the atoms, the difference between chemical compounds and adsorption compounds will probably be less marked than it is now. At least, we hope that it will be possible to account for all phenomena, physical and chemical, by calculating the forces between the molecules and electrons and atoms. If those atoms are all electrical in nature, the force holding the atoms together in a chemical compound such as NaCl and the force binding argon atoms at the surface of charcoal, would be of the same nature. . . .

"Langmuir's theory of adsorption involves the assumption that the forces acting in adsorption are of nearly the same kind as all forces causing chemical combination. From the point of view of the modern conception of the atom, we might say that atomic forces seem to be developed from the deviations of the orbits of the outer electrons in the atoms. The forces acting in ordinary chemical compounds would be due to very strong deviations of those orbits. In adsorption phenomena the forces acting should be due to comparatively small deviations. When we come to measurements of adsorbed gases at high pressures, we find considerable deviation from the values calculated from Langmuir's formula.

"The basis for Langmuir's theory is that on the surface of a crystal there are a certain number of what he calls elementary spaces, points where there is residual valency. The forces acting in adsorption are concentrated at those points and adsorption consists of a fixing of the adsorbed atoms in the elementary spaces for a certain time, the average life of an adsorbed atom or molecule on the surface. He also assumes that those spaces can, as a rule, hold only one atom or molecule, *i.e.* that the adsorbed layer is only one molecule thick. That means that the force between the atoms of the surface and the atoms of the adsorbed substance decrease rapidly with the distance between the atoms. They will only act when the atoms are very close together. He arrives at an expression between the concentration in the solution and the adsorbed quantity by assuming that there is equilibrium between the rate of adsorption and the rate of deadsorption, or in the case of a gas the rate of condensation on the surface and the rate of evaporation. . . .

"Another adsorption theory which I would like to mention is one representative of quite the opposite point of view and that is the Eucken-Polányi theory. The leading ideas in this theory were first published by Eucken and then worked out by Polányi. The basic assumption is that the adsorbed layer does not consist, as in Langmuir's system, of a single layer of atoms or molecules, but it consists of a polymolecular laver with a density varying continually from the adsorbing surface out into the free gas or liquid— a sort of an atmosphere of adsorption. He assumes that the condition near the surface is like the atmosphere around the earth. At every point, we can define a function that expresses what he called the adsorption potential. By this, we mean the work done by transporting the mass unit of the adsorbed substance from the point in question to infinity. By means of the adsorption potential and by the van der Waals' equation, or, in the case of very low pressures, the simple Boyle's law, he has actually been able to account for adsorption phenomenon in gases. Experimental evidence at present is not sufficient to decide which of those theories will prove to be the most useful one. In certain cases, perhaps, the Polányi point of view will be the most suitable one, but, on the whole, Langmuir's theory gives a more defininite formula, and is easier to prove experimentally."

The reviewer was very much interested in the discussion of cataphoresis, p. 197. "One might be inclined to assume that the potential difference displayed in cataphoresis is the same one as the substance of the particle would show when used as an electrode in a galvanic cell. A metallic particle immersed in a very dilute solution of one of its own salts would then give a potential difference according to its solution pressure.

"A few years ago some scientists actually held the above view and Billiter tried to determine the absolute zero potential by means of a method based upon such an assumption. We know now, however, that the potential difference which causes cataphoresis is not the same as the interface potential between the particle and the liquid, as measured in a galvanic cell. An experiment in favor of this view is that the electrokinetic potential difference is changed by the addition of ions—especially such ions as are strongly adsorbed, and it is therefore natural to assume that this potential difference is to a large extent due to the difference in adsorbed charges—to the different adsorption of ions.

"Freundlich and his co-workers have thrown some light upon this question. They have measured statically the potential between the surface of the particle and the liquid, and also determined the electrokinetic potential for the same substance. Take for instance a glass tube and blow a very thin bubble at the end. Then immerse it in a solution and fill the inner part with an electrolyte. The interior of the glass bubble is connected to one side of an electrometer by means of a platinum wire and the outer liquid to the other side over a reversible calomel electrode. This combination enables us to measure the potential difference between the interior of the glass and the outer liquid. Freundlich also measured the electro-kinetic potential for the same kind of glass by measuring the streaming potential in a capillary. In that way, he found that the interface or static potential between the glass and the liquid is higher than the electrokinetic, and that the interface potential is not affected by small additions of ions which cause a very great change in the electrokinetic potential difference.

"In order to explain why the electrokinetic potential is so much smaller than the static one, Smoluchowski assumed that part of the liquid is carried on with the particle in its movement, and that the potential difference we measure in cataphoresis is, therefore, that from a point out in the liquid to the infinity point. If this is actually the case, it is possible to explain how the small additions of electrolytes can affect the electrokinetic potential without affecting the other potential, and that such additions can even reverse the sign of the potential."

This is very ingenious; but it proves too much. The flowing-mercury electrode is evidently the reverse of cataphoresis and should therefore give the same value obtained by Billiter and by Garrison if Smoluchowski were right.

Through rather non-committal as to Loeb's theories, there is a statement, p. 204, that "when we try to apply the Donnan equilibrium to the single particles in sols as has been done by Loeb we meet with certain difficulties which have not as yet been overcome. The main difficulty is that the two regions of different concentration have no tangible meaning."

"The coagulating action of two or more electrolytes present at the same time is not additive as in the case of a hydrophobe sol such as gold. If we measure, say, the coagulation value of KCl in presence of various amounts of LiCl, we shall find that in certain concentrations of LiCl it takes more KCl to coagulate the sulphur than when there is no LiCl present. Odén believed that this antagonistic action between the two electrolytes was due entirely to the antagonism between the cations and the anions. According to recent experiments by Freundlich there is probably also an antagonistic action taking place between the different cations. He found that the coagulative power of cations of high valency is reduced quite enormously by the presence of, say, Li_2SO_4. In a Li_2SO_4 solution containing 65 percent of the concentration necessary to coagulate the sulphur, it was necessary to raise the concentration of $CeCl_3$ to 150000 percent of the coagulation value in a lithium-free sol in order to get coagulation. Such a phenomenon can hardly be ascribed to the peptizing action of the anions only," p. 224.

It is interesting to note, p. 238, that when a jelly swells, the energy represented by mechanical work as done by swelling is almost exactly equal to the heat change. In other words, "the heat of dilution of a gel is almost exactly equal to the energy represented by the work of swelling. This means that the mechanical work performed by a swelling gel is surprisingly economical. Now probably most of the muscular work is performed by swelling of gels, and it is remarkable that it has been found by physiologists that a very large amount, at least 60 percent, of the heat produced by the body can be transformed into mechanical work of the muscles."

This is a very valuable book and the scientific community is indebted to the University of Wisconsin for bringing Professor Svedberg to this country and for making these lectures possible. It is very difficult to judge such a piece of work objectively; but it seems to the reviewer that a possible criticism is that Svedberg is rather more interested in the mathematical formulations than in the underlying principles. A case in point is the comment on the work of Burton and of Porter, p. 101. There is no doubt that the Einstein formula, as used by Perrin, is not adequate to describe the distribution of a sol under the influence of gravity; but Svedberg hates to admit it.

Wilder D. Bancroft

The Chemical Basis of Growth and Senescence. *By T. Brailsford Robertson. 21 × 15 cm.; pp. viii + 389. Philadelphia: J. B. Lippincott Company, 1923. Price: $3.00.* In the preface the author says: "Each successive acquirement enlarges our power to grasp more, and the progress of human knowledge is, in fact, autocatalyzed. Thus, if at the present moment we are not in a position to interpret fully the phenomenon of life, that is ground for hope rather than despair. We can see fairly clearly what type of physical and chemical knowledge will be requisite for this interpretation, and we realize that the merest rudiments of this essential knowledge have been acquired so recently that they are yet unfamiliar tools, of which the consequences are barely apprehended. In this volume, a preliminary essay has been made towards that interpretation of development which M. Bergson declares to be intellectually impossible."

The chapters are entitled: introduction; the physical manifestation of growth in man; the physical manifestations of growth in animals and plants; the reproduction of unicellular organisms; the substrates of growth—inorganic salts and amino acids; the substrates of growth—accessory food factors; the retarding influences in growth; differentiation and development; the nutrient level in relation to growth; hyper-differentiation—cancer; the influence of special agencies on growth; growth and evolution.

In the case of man the author differentiates pre-natal, post-natal (or infantile), juvenile, and adolescent cycles of growth, pp. 16, 26, 41. "The fact that each growth-cycle begins slowly and increases progressively in velocity until the moment of maximal growth-velocity is attained at the centre of the cycle, is sufficient in itself to show that the process of growth is autocatalyzed", p. 6. "This being the case, the question immediately presents itself why the process of growth, since it is self-accelerated, ever comes to a stop? In other words, why do plants and animals not grow with ever increasing velocity to dimensions indefinitely great?," p. 8.

In the case of unicellular organisms, p. 101, "we have seen that the autocatalytic character of growth is attributable to the autocatalysis which occurs during nuclear synthesis; that the accelerative agent which is responsible for the auto-acceleration of nuclear synthesis is in part retained within the nucleus, and in part shed into the surrounding medium, and, finally, that during the lag-period, before any cell-division has occurred, the nucleus is insensitive to accelerative agents in the surrounding medium, other than the indirect and comparatively slight acceleration due to the mere abundance of foodstuffs.

"These considerations, taken together, unite in indicating pretty clearly that the moment of distribution of the accelerative agent between the nucleus and the surrounding medium is that at which cell-division or the preceding nuclear division occurs. And this is, indeed, a very reasonable assumption for the nuclear membrane is known to be relatively impermeable to many soluble materials and the dissolution of the nuclear membrane which accompanies nuclear division may well render possible a redistribution of nuclear materials between the nucleus and the cytoplasm, and the admixture of nuclear material with those constituents of the pericellular fluid which are capable of penetrating cytoplasm."

"The inorganic substrates of growth must evidently comprise all of the inorganic elements which are found in adult tissues. The essentiality of some of these has long been well established. Thus the experiments of Abderhalden have shown that if rabbits are maintained upon a diet deficient in iron, by continuing milk feeding after the normal period of lactation, they fail to grow at the normal rate and display anaemia, quantitatively measurable by the decrease of relative haemoglobin content. Addition of inorganic salts of iron greatly improved growth, but did not alleviate the anaemia because certain substances necessary for the utilization of iron to manufacture haemoglobin were not supplied in sufficient abundance by milk. Hence iron, possibly in association with nucleo-proteins, plays some other rôle in the body besides that of enabling the manufacture of haemoglobin. Addition of green forage containing iron speedily corrected the anaemia. There is thus a daily wastage of iron from the body which must be replaced by a current supply in the dietary.

"The necessity of iodine for the manufacture of the active constituents of the thyroid (thyroxin) is manifested in the disorders of thyroid functions which supervene when the nutrient supply of iodine is deficient. That lack of iodine in the dietary may actually lead to hypofunction of the thyroid, is demonstrated by the preventive effect of frequent administration of small doses of iodides. Under circumstances which throw excessive strain upon the thyroid, such as the pollution of water by certain micro-organisms, then even the normal proportions of iodine in the dietary may be inadequate, and under such conditions the administration of iodides does not seem to be so effective in preventing hypofunction of the thyroid, as it is when the disorder arises from simple inadequacy of the iodine in the dietary. It is not clear how and for what reason a wastage of iodine occurs from the body, entailing a continual renewal of this element.

"In respect to other inorganic elements our information is more meagre. The necessity of lime and phosphates for the growing animal is evident from the fact that the former substance enters extensively into the formation of bone, while phosphorus is required for the manufacture of all nuclei and of the lipins which abound in all tissues and more especially in nervous tissues. Accordingly, Osborne and Mendel have found that young rats fail to grow if deprived of lime and phosphates and that considerable proportions of these substances are requisite to maintain a normal growth-rate.

"In respect to the remaining mineral constituents of protoplasm, Osborne and Mendel have shown that *either* sodium or potassium must be abundant in the diet, but provided potassium is abundant sodium may be reduced to 0.04 per cent of the intake, while if sodium is abundant then potassium may be reduced to 0.03 per cent. No more than 0.04 per cent. of chlorine and 0.01 per cent. of magnesium are required to maintain growth," p. 109.

"On the other hand the majority of the naturally occurring proteins contain all of the dietary amino-acids, although in widely varying proportions. Only in a few exceptional classes of protein do we find that certain amino-acids are lacking. Gelatin is a well known example of an incomplete protein lacking cystine, tyrosine and tryptophane, and it has long been realized that gelatin is not in itself an adequate protein for the maintenance of nitrogenous equilibrium, although it is a "sparer" of protein, *i. e.*, can furnish a portion, but not the whole of the protein in the diet. This, however, is not conclusive evidence of the inability of the tissues to synthesize some amino-acids for others, for cystine being the only amino-acid which contains sulphur manifestly cannot be synthesized from any other. In recent years, however, the researches of Willcock and Hopkins and of Osborne and Mendel have established the fact that certain other proteins lacking one or other of the amino-acids are similarly inadequate to maintain nitrogenous equilibrium or permit growth. Thus zein, the alcohol-soluble protein in maize, which lacks tryptophane, lysine, and glycocoll, is inadequate to maintain nitrogenous equlibrium unless it is supplemented by tryptophane, and even with this addition it will not support growth. Since glycocoll can be synthesized by the tissues, the limiting factor, when zein has been thus supplemented, must of course be lysine. Gliadin, the alcohol-soluble protein in wheat and rye, contains tryptophane but is lacking in lysine and glycocoll, and this protein permits the maintenance of protoplasm already synthesized, but, like zein which has been supplemented with tryptophane, it fails to support growth. We may therefore infer that tryptophane and lysine are both capable of becoming limiting factors of growth when they are lacking or present in inadequate amounts in the diet," p. 113.

"Summing up, therefore, the present state of our knowledge concerning the amino-acid requirements of the higher animals, we may state that cystine, tryptophane and either histidine or arginine are necessary both for growth and for the maintenance of tissue already manufactured. Lysine is essential for growth but not for maintenance. Glycocoll is not essential for either purpose since it can be manufactured, directly or indirectly, from other amino-acids. Regarding the thirteen amino-acids which remain, our ignorance of their necessity or replaceability in the diet is almost complete, although Abderhalden suggests that proline may be derivable from glutamic acid and arginine from ornithine," p. 119.

"The fat-soluble accessory is essential for the growth and reproduction of animals. Adult rats are able to withstand the absence from their diet for over a year without loss of weight, but if previously, in the growth period, they have been confined to a diet deficient but not altogether lacking in it, then subsequently, when they are nearly adult, deprival causes, after some delay, a sudden decline of weight and ultimate death from apparent inanition or from intercurrent disease. When young animals which have hitherto received normal nourishment are suddenly deprived of this factor they continue to grow for a considerable period, but growth cannot be sustained and arrest of growth is followed by progressive loss of weight. An amount of the factor which is just adequate to permit growth may not suffice to permit reproduction and it is not supplied to suckling young unless the mother is also receiving it. These facts unite in pointing to an ability on the part of animals to store up reserves of this factor in their fats, upon which they are able to draw in order to supplement temporary deficiencies in the ration, so that with this assistance an allowance of fat-soluble factor which would not by itself suffice for the animal's requirements, may remain adequate until the accumulated stores have been depleted, when its inadequacy is revealed either in the animal itself or in its offspring," p. 124.

"The circulating nitrient fluid of the *Vertebrata*, the blood, may therefore be conceived as a reservoir of foodstuffs which is maintained at a constant level by three main types of process. An *inflow* due to the assimilative activities of the digestive tract, an *outflow* into the tissues originating in their needs for growth, repair or maintenance, and an *overflow* which is secured by storage in the case of fats and carbohydrates, and by deaminization in the case of protein. Thus any lack of equivalence between inflow and outflow is offset by the overflow. As in the case of the other instances of environmental invariance discussed above, uniformity of the nutrient environment is achieved by a series of dynamic equilibria involving the coordinated participation of many tissues. Its success is of course dependent upon the ultimate satisfaction of appetite by food, but even at the point of death from starvation the blood is found to contain elementary nutrient constituents," p. 233.

"It will be observed that those organs which are most essential to the preservation of existence are those which suffer least extensively from the deprivation of food. This must be due to some definite peculiarity of the metabolism of those tissues which are able to maintain their weight under these adverse circumstances. The nature of this peculiarity may easily be inferred from the fact that the speed of metabolism is exceptionally great in just those tissues, the heart and nervous system, which most successfully resist the distintegrating effect of inanition. Thus the heart is constantly engaged in transforming large amounts of potential energy into mechanical work and yet it carries within itself an extraordinarily small reserve of energy-yielding materials. The glycogen-content of the muscular tissues of the heart, instead of being exceptionally high, is, as a matter of fact, no higher than that of the skeletal muscles, which are only contracted intermittently. The heart must thus depend, for the maintenance of its exertions, upon the direct and unceasing withdrawal of nutrient materials from the circulating fluids. In so doing it is forced to compete with all other tissues of the body, and yet it does so with so much success that whereas the majority of the other tissues lose a very considerable part of their weight, the heart maintains the integrity of its substance until death is imminent. This implies that the rate of utilization of nutrients by the heart must greatly exceed that of the other tissues, so that foodstuffs are appropriated by it in advance of the ability of other tissues to consume them," p. 250.

"If, however, the administration of tethelin is confined to the preadolescent period, results of a very different character are obtained. These effects may be elicited by administering tethelin (4 milligrams per day) from the fourth to the twelfth weeks of age and then discontinuing the administration. The curve of growth of these animals in comparison with that of normals is shown in the accompanying chart, and their external appearance at 500 days old is compared in the accompanying photograph. The increase of bodily dimensions is extraordinary. The *average* weight of the treated females at 500 days was 31 grams, while that of the normal females was only 25 grams. An increase of 25 per cent. in average weight was thus obtained corresponding in human females to an increase from the *average* normal weight of about 120 lbs. to an average weight of 150 lbs. But the average was considerably diminished by a small proportion of animals which failed to respond to the treatment, while one-eighth of the treated animals exceeded 40 grams, a weight which would correspond to 190 lbs. in the human female and which, in our experience of over a thousand animals, has never been attained by any normal female, and only once or twice by females receiving cholesterol. These results, obtained by the administration of but 4 milligrams of material daily for eight weeks are comparable with those obtained by Uhlenhuth in *Amblystoma* by administering a diet consisting entirely of pituitary (anterior lobe) tissue. The experiment has been repeated, employing males, and with a similar outcome.

"The origin of these gigantic proportions lies in an excessive late accretion of tissues and gigantism is not displayed in its full degree until the animals attain the age of 500 days, or over a year after the discontinuation of the administrations. Corresponding to this we find, in accordance with the general rule that late accretion of tissues is unfavorable to longevity, that the duration of life in these animals was abbreviated rather than enhanced," p. 299.

"Our analysis of the phenomena of growth has led us to the conclusion that the diversity of cells originates in a diversity of relationships between nucleus and cytoplasm. The communal life of the metazoa, and to a lesser extent that of the multicellular plants, led to the acquirement of a certain degree of independence of short-period fluctuations in the nutrient environment, and a relative constancy of the nutrient level in the pericellular fluids. In this way the first step was taken towards the evolution of the communally-controlled environment which is exemplified in its most elaborate form in the homoiothermal animals . . .

"But the acquirement of environmental invariance carried with it the penalty of mortality imposed by the pericellular accumulation of the nuclear autocatalyst. Mortality, however "disadvantageous" in a personal sense to the individual, was of no disadvantage to the race, for gametic reproduction ensured its continuance," p. 309.

"The stasis of growth which is imposed upon multicellular communities by the accumulation of autocatalyst in the pericellular fluids is deferred for a longer or shorter period by the step-by-step reduction of the nuclear ratio at division, whereby nuclear synthesis is enabled to proceed because it is periodically reinaugurated by the discharge of autocatalyst into the medium. For this too a penalty has to be paid in the loss of genetic characters consequent upon diminution of the nuclear content at each successive differentiation. The differentiated cell bears a mutilated germ-plasm. When the utmost degree of differentiation has been attained, then stasis can no longer be deferred and the ultimate consequence is senescence and the termination of the existence of the individual," p. 310.

Wilder D. Bancroft

Recent Developments in Atomic Theory. *By Leo Graetz. Translated by Guy Barr. Fourth edition. 22 × 15 cm; pp. xi+17. New York: E. P. Dutton and Company, 1923. Price: $3.50.* The book consists of six lectures, entitled: molecules and atoms in chemistry and the kinetic theory of gases; atoms and ions and electrical effects in liquids and gases—atoms of electricity; the disintegration of atoms in radio-active substances—the nucleus theory of the atom; X-ray spectra and the nucleus theory of the atom; line spectra and Bohr's model of the atom; further investigations on the structure of nuclei, atoms, ions, and molecules—decomposition of nuclei.

The first lecture ends, p. 24, with the interesting statement that the conclusion may be drawn from the multiplicity of lines in the spectra of elements, that the atoms cannot be simple bodies, but must contain parts of some sort, *i. e.* that they cannot really be 'atoms'

"The curious phenomena of α-particles, their sudden stoppage after traversing their range, their usually weak scattering and their unusually strong deflections are explained, as Rutherford showed, if we assume that an atom consists of a postively charged nucleus of extremely small volume around which, at a distance corresponding roughly with the atomic radius, are negative electrons sufficient to make the whole atom neutral. These negative electrons are either at rest or revolve round the nucleus like planets round the sun. An α-particle, whose dimensions must be supposed very small, will generally shoot through the atom somewhere in the interspace between the positive nucleus and the electrons, and will only experience a small deflection which is the resultant of the repulsion from the nucleus and the attraction by the electrons; this is small because, in its flight through the atom, the α-particle moves at a relatively great distance from the nucleus and from the electrons. It may happen, however, that an α-particle flies directly towards a negative electron or, in rarer cases, directly towards the positive nucleus. In the former case it will combine with the negative electron and change from a helium atom with two positive charges to one with a single charge, and if it then meets yet another electron it will become a neutral helium atom. According to the velocity of the α-particle this will happen sometimes earlier, sometimes later. But once this neutralization of its charge has occurred the helium atom suddenly loses its property of ionization and thus is explained the sudden stoppage of the α-rays after they have traversed their range.

"On account of the assumed smallness of the nucleus it will very much more rarely happen that an α-particle is projected into the immediate neighborhood of the nucleus of the atom. When this occurs there will be a strong repulsive force between the positive charges of the α-particle and of the nucleus, and the α-particle must be deflected at a sharp angle (more accurately in a hyperbola) from its path. In this manner are explained the two phenomena which are so striking and at first so mysterious, the sudden stoppage of the α-rays and their occasional sudden deviation, phenomena which at first appeared to baffle explanation," p. 73.

When X-ray spectra are obtained with crystals, the wave-lengths of X-rays used can be determined from the figures produced, p. 95. "The different diffraction spots were shown to be due to wave-lengths of different values present in the non-homogeneous X-radiation used, and calculation indicated that in the X-rays employed there were wave-lengths varying from 0.3 to 1.5 A.U. The waves are from 600 to 3000 times smaller than those of the most extreme ultra-violet which has yet been produced and measured, in which the wave-length is still 1000 A.U."

"Every metal, when used as anticathode in a bulb, shows similar lines of definite wave-length. Experiment has shown that the wave-lengths of these characteristic lines are the shorter, the higher the atomic weight of the metal concerned is. It has further been demonstrated that the lines for the lighter elements from sodium to neodymium have all the same structure. They are called the K-lines of the K-spectrum. They consist always of five lines which are distinguished as $K\alpha_1$, $K\alpha_2$, $K\beta_1$ $K\beta_2$ and $K\gamma$; of these the lines $K\alpha_1$ and $K\alpha_2$, which are close together, are the strongest. The β-lines similarly form a doublet, and in some substances the γ-line is also double. These lines are present with all the substances mentioned. If the cathode consists of an alloy, e. g. brass, the lines of both constituents, copper and zinc, appear together on the plate. Even if the anticathode is simply covered with the salt of a metal the lines of the constituents are shown, e. g. potassium chloride gives the lines of chlorine and of potassium.

"With the heavier of these elements, from zinc onwards, a second system of lines is found, distinct from the first, with wave-lengths considerably higher than those of the K-lines. This is known as the L-spectrum. It consists of from ten to fourteen lines, the strongest of which is called the $L\alpha_1$ line. Here again the wave-length of the lines diminishes with increasing atomic weight. Among the heaviest elements, from neodymium up to uranium, only the L-series has hitherto been found and not the K-series. On the other hand, for the heaviest elements of all, from dysprosium to uranium, a spectrum has been found with still longer waves; this is the M-spectrum, and consists of from three to five lines, some of them doublets," p. 100.

"According to Prout's theory as now interpreted, there can be no necessity for atomic weights being exactly whole numbers. For the atomic weight is composed of the masses of the nucleus and of the negative electrons, and, moreover, all these masses are apparent. Now even though the apparent mass of a negative electron is only 1/1835 of the mass of a hydrogen atom, it is to be expected that if many of these negative electrons are present in and outside the nucleus, small deviations from whole numbers will occur for the atomic weights. Another point follows. If the negative electrons outside the nucleus are in motion and their velocity happens, in some particular atom, to be very large, i. e. comparable with the velocity of light, then their apparent mass would also be greater, and under these circumstances even considerable deviations of the atomic weights from whole numbers could occur. Thus the objection to Prout's hypothesis, which was rightly raised at an earlier stage, has here no longer any force, for the number of negative electrons in and outside the nucleus may in some circumstances be considerable. Again, the mass of a hydrogen nucleus depends to some extent, since it is apparent mass, on whether other positive or negative charges are in its immediate neighborhood; it may accordingly be either greater or smaller. This is another reason for possible small deviations of the atomic weights from whole numbers either upwards or downwards. In short, there is no longer any valid objection to the supposition that all atoms are composed of protons and electrons," p. 115.

With sound waves "the difference in frequency between successive overtones in any octave is always the same, namely one, being equal to the frequency of the fundamental. If this were the case with the vibrations which give rise to the line spectra, the separate lines of a diffraction spectrum, expressed as frequencies, would all be equidistant from one another, except for some which might be missing from the series. This is far from being the case, so that analogy with sound vibrations leads to no result in the investigation of line spectra," p. 122.

"It is evident, from what has been said, that Bohr's model of the atom embraces, in a very simple manner, a number of important and remarkable experimental facts. The explanation of the series lines, in particular the complete explanation of Balmer's series for hydrogen, the derivation of Rydberg's constant, and the deduction of Moseley's law for X-ray spectra, are very striking achievements of this theory of the atom. There are, however, many experimental facts which still await more detailed explanation on this theory. In particular, there are a number of regularities which have been found in the series spectra of the alkali and alkaline earth metals, and other also which have been observed in the action of a magnetic field on the series lines (known as the Zeeman effect) which still requires accurate explanation by this model. On the other hand, the action of an electric field on the series lines (known as the Stark effect) can be quite completely elucidated by Bohr's model of the atom. For the rest, it should not be overlooked that there are several arbitrary assumptions made by Bohr, which only served to derive Balmer's series. According to our present knowledge of electricity an electron cannot, in general, continue to rotate in a circle about a nucleus; for it is giving up energy to the ether all the time and must, in consequence, gradually fall into the nucleus. But Bohr's theory supposes that, in the orbits described, no radiation of energy into the ether takes place. For this assumption, as for a number of others, there is no *a priori* foundation; it is warranted only by its splendid result, the explanation of the series lines, and by the fact, which is incontrovertible, that in the domain of the atom, at minimal distances, the laws of mechanics and electro-dynamics which we have found elsewhere are not of general validity," p. 147.

"Although the constitution of the higher atoms cannot be settled in individual cases, it may be postulated as probable that the production, of a molecule from two atoms of the same or of different kinds takes place, in general, as it does with hydrogen, by the formation of a common ring about the two separate atoms; this ring is what causes the combination of atoms into molecules. And, of course, it is to be assumed that in all molecules it is the outermost electrons, electrons of the outside ring, which so link up to form the molecule.

"If we now consider the different effects of physical and chemical forces upon atoms according to these methods of representation, and examine how these effects are expressed, we have the following list:—

(1) Chemical phenomena take place essentially in the outermost rings of the atoms. These outermost rings fuse together and cause the production of the chemical molecule.

(2) The action of very high temperatures on the one hand, and of electrical excitement (in Geissler tubes) on the other, also affects the outer rings, and in many cases the inner as well, by breaking them up so that their re-formation produces the ordinary spectra.

(3) The bombardment of the electrons occasioned by X-rays influences principally the innermost rings of the atoms, which it destroys. By their re-formation the K-, L- and M-rays of the X-ray spectra result.

(4) Finally, the nuclei of the atoms are themselves concerned in radio-activity. The nuclei of the heaviest atoms disintegrate spontaneously and emit α- and β-rays. The concomitant γ-rays may, according to Rutherford, be regarded as the characteristic X-rays of the respective radio-active materials. The α-particles also decompose other nuclei, as has been shown with nitrogen.

"Thus radio-activity invades the innermost part of the atom, its nucleus, and effects a real transmutation of atoms. For on the Rutherford-Bohr theory, a particular atom is characterized only the the charge of its nucleus. The number of electrons revolving about the nucleus depends on circumstances and merely distinguishes between the neutral atom and the positive or negative ion of the atom. But a change in the nucleus produces a new atom. Up till now we have not been able to influence this change of the atom by any means at our disposal. Either it takes place of itself, spontaneously, as in radio-active substances, or it does not take place at all. By the new researches of Rutherford, which we have mentioned, the first step has been taken in the direction of interfering with it as we please. And if, as is to be hoped, this beginning is further developed, if we can use means to interfere with and to modify the changes, if we can make this disintegration of the nucleus quicker or slower and if we can extend it further to other atoms than hitherto, then this superchemistry, the chemistry and physics of the nucleus of the atom, the manifold application of which to science we have here discussed, will have practical results beyond expectation," p. 169.

The author, being a physicist, discusses Bohr's conception of the atom at great length. Langmuir's name occurs once, p. 164, quite casually and Lewis is not even referred to.

Wilder D. Bancroft

Interfacial Forces and Phenomena in Physiology. *By Sir William M. Bayliss 19×13 cm; pp. ix+196. New York, 1922. Price: $3.00.* This volume is based on the Herter Lectures given in New York in March, 1922. The chapters are entitled: heterogeneous systems; surface tension; adsorption; colloids; haemoglobin; enzymes; the cell membrane; electrical phenomena in living cells; protoplasm; muscle, nerve and gland; general remarks.

Bayliss adopts the view of Clowes as to emulsification by calcium and sodium soaps, p. 26, which is good; but he evidently thinks that a semipermeable membrane is one with small pores, p. 13, which is bad. The experiments on dyeing filter paper with Congo red, p. 49, fit in beautifully with the modern theory of dyeing. There is also the interesting statement, p. 56, that "addition of alcohol increases the adsorption of an acid dye, decreases that of a basic dye. The explanation of this behaviour is obvious. The negative charge on the paper is diminished by alcohol because of its lower dielectric constant than that of water."

Bayliss does not agree with all of Loeb's views, p. 67. "The opposition made by Prof. Jacques Loeb between what he calls "colloidal" chemistry and "classical" chemistry is a puzzle to me. At first, it seemed that theories relating to heterogeneous systems were to be excluded from application to colloids. But we find osmotic pressure and the Donnan membrane equilibrium freely made use of in Prof. Loeb's work. It might indeed seem to some that the latter is strained to breaking point. Also, phenomena due to aggregation, while not looked upon with favour, are recognized. Finally, the only difference turned out to be the existence of adsorption which is not to be mentioned in the discussion of colloids. We have seen reason to believe in its genuine occurrence where surfaces are present, and these must be present if there is such a thing as aggregation of molecules to form particles. We shall see reason to accept this even in the case of proteins. The purely chemical properties can scarcely differ much, if at all, when molecules or ions are joined to form masses; but the physical properties do, and these are of much physiological importance. It is only necessary to mention viscosity, surface tension, osmotic pressure and so on, even if we omit adsorption."

From the fact that it is difficult to squeeze water out of a gelatin jelly before treatment with formaldehyde and easy to do so afterwards, the author concludes that the structure has changed from a honeycomb one to an interlacing one. This may be true; but it does not follow necessarily. There may have been a change in the adsorptive power of the gelatin.

Of special interest is the author's suggestion, p. 134, that the cell membrane may be permeable at one moment and semi-permeable at another. "It is a matter of great difficulty to suggest any probable structure for the membrane. Owing to its mode of production, it is no doubt of a very complex chemical nature. It appears to be in all states of the cell permeable to all substances soluble both in water and in oil or liquid, such as urea, some ammonium salts, alcohol, chloroform, carbon dioxide, oxygen, etc. as Meyer and Overton pointed out. In the resting state of the cell, the membrane is impermeable to salts, other than certain salts of ammonium, to glucose and to amino-acids; while in a state of activity it becomes permeable to all these."

The reviewer would have welcomed a fuller discussion of the behavior of the contractile vacuole, p. 137. "But in cases such as those of protozoa in water, there is a continuous intake of water which would burst the cell were it not for the periodic rejection by the *contractile vacuole*, as was first pointed out by Marcus Hartog. As this vacuole grows in size, it reaches the cell-membrane and empties itself, the membrane then closing over the orifice. The whole process is repeated periodically."

Most physical chemists will balk at the author's definition of the eutectic temperature, p. 163, as the temperature at which any solution solidifies together of a uniform composition. A eutectic composition is also necessary.

Wilder D. Bancroft

THE ELECTROLYTIC THEORY OF CORROSION[1]

BY WILDER D. BANCROFT

About every so often in the development of a theory, it is necessary to stop and take account of stock. The original propounder of the theory may have been considering a special case and may not have worded his theory in the best possible way, or a new set of facts may have been discovered which had not been foreseen. The supporters of the theory may have over-emphasized certain applications of the theory until people mistake these for the theory itself. Unless people are on their guard, which they rarely are, the theory will change in passing through many hands until it is scarcely recognizable. This is the more likely to happen when, as is usually the case, people do not bother themselves with the historical development. Some or all of the things have happened to the electrolytic theory of corrosion and Messrs. Bengough and Stuart[2] concluded that corrosion may be either chemical or electrochemical. Since many of their conclusions are based on what seem to me misapprehensions of fact and misunderstandings of the electrolytic corrosion theory,[3] it has seemed worth while to formulate the electrolytic theory of corrosion as I understand it, and to show how it should be applied in a number of special cases. This is the more necessary because it must be admitted that the supporters of the electrolytic theory of corrosion have too often played into the hands of their opponents and have not made the most of the material available.

The first formulation of the theory of electrolytic corrosion was made by Whitney.[4] "Practically the only factor which limits the life of the iron is oxidation, under which are included all the chemical processes whereby the iron is corroded, eaten away, or rusted. In undergoing this change, the iron always passes through or into a state of solution, and, as we have no evidence of iron going into aqueous solution except in the form of ions (probably electrically charged atoms), we have really to consider the effects of conditions upon the potential difference between iron and its surroundings. The whole subject of corrosion of iron is therefore an electrochemical one, and the rate of corrosion is simply a function of electromotive force and resistance of circuit. If now we apply Nernst's conception of the source of electromotive force between a metal and a solution, we must conclude from the measured potential difference that iron in contact with an aqueous solution tends to

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[1] A report to the Corrosion Committee of the National Research Council. The cost of some of the experiments on which this report is based was met by a grant from the National Research Council and by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 31 (1922).

[3] Dunstan and Hill: J. Chem. Soc. 99, 1857 (1911).

[4] J. Am. Chem. Soc. 25, 394 (1903).

dissolve, ionize, or oxidize with a force expressed as equivalent to about 10,000 atmospheres' pressure at ordinary temperature.

"In other words, iron should tend to dissolve in any aqueous solution[1] until the concentration of the electrically charged iron ions reaches such a concentration that the osmotic pressure is equal to the above value. This means that the saturated iron solution must be at least 450-fold normal, which is a concentration not practically obtainable. Thus far the theory requires that iron should *tend* to oxidize in any aqueous solution. Whether it will do so or not depends on other conditions. Something may here be gained by a study of analogies. The dissolving zinc electrode of the Daniell or gravity battery, although possessing an enormous electrolytic solution pressure, does not dissolve when the electric circuit is broken, but begins oxidizing immediately when connected through any external resistance to the copper pole. It is not enough then for oxidation or solution of the metal, that it have a *tendency* to dissolve; it must be in metallic connection with some other material capable of acting as an electrode, and this second electrode, if a positive element, must have a lower electrolytic solution pressure than the iron. Iron in contact with zinc and an aqueous solution will therefore not dissolve; but if copper replace the zinc, the iron will dissolve, the velocity of solution in these cases being determined by the resistance of the complete electric circuit. These two cases are often met with in practice. In marine boilers, zinc plates are sometimes suspended from the boiler tubes in the water, that they may be attacked instead of the iron. On the other hand, scrap iron is used very commonly to recover copper from solution in mine waters and other copper liquors in which case the iron rapidly dissolves.

"Hydrogen acts as a metal and is electrolytically classified in the group with copper when compared with iron and zinc. That is, if a cell were made up on the Daniell model, iron being used instead of zinc, and hydrogen in place of copper, the cell would generate a current when the iron and hydrogen electrodes were connected. Iron would then dissolve with a velocity dependent on the total resistance of the circuit. So also, and for the same reason, iron when placed in a solution containing hydrogen ions will dissolve as the hydrogen precipitates, just exactly as when placed in the copper salt solution. That iron does oxidize or dissolve in all solutions containing appreciable quantities of hydrogen ions is well known. This electrochemical relationship between iron and hydrogen is the primal cause of rusting."

These paragraphs contain the substance of the theory of electrolytic corrosion and are just as true today as they were twenty-one years ago, except as to absolute values. In two respects, however, the wording is not as happy as it might have been. At the time that Whitney wrote, it was still believed by many that we knew the single-potential difference between a metal and a solution with a fair degree of accuracy, whereas nowadays we know that we do not. Consequently we cannot calculate the absolute value of the solution pressure; but it is immaterial for the argument whether this value is equivalent to 5000, 10000, or 20000 atmospheres pressure. The value is larger than

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[1] [In pure water the limiting solubility will be that of hydrous ferrous oxide. W. D. B.]

that for hydrogen, which is all that is of importance. While it is true that iron should tend to dissolve in any aqueous solution until the concentration of the electrically-charged iron ions reaches such a concentration that the osmotic pressure is equal to the solution pressure, Whitney has neglected to state that this will only be true so long as the iron is kept electrically neutral. If the metallic iron becomes charged negatively because of the formation of positively charged ferrous irons, there will be set up an electrostatic field which will prevent further formation of ferrous ions. This may happen even when the concentration of ferrous ions in the mass of the solution is practically negligible.

This point was brought out clearly by Nernst[1] and by Whitney[2] in his translation of LeBlanc's book. "In order to explain the production of a potential difference through the contact of a solid substance with a liquid, imagine a metal dipped into pure water, and that a certain amount of metal ions is produced owing to the electrolytic solution pressure. The metal at the same time becomes negatively electrified, since both kinds of electricity must be simultaneously produced whenever electrical energy comes into existence. The solution is thus positively electrified and the metal negatively, and there is formed a so-called double layer. The ions sent into the solution with positive charges and the negatively charged metal attract each other; in other words, a potential difference is produced. The solution constantly tends to send more ions into solution, while the electrostatic attraction of the electrical double-layer opposes this action, and evidently equilibrium is reached when the opposing tendencies are equal. Since the ions have very high charges of electricity, this condition of equilibrium occurs before weighable quantities of the ions have passed into the water."

Whitney undoubtedly did not discuss this point in detail because he assumed that it was familiar to everybody; but people nowadays are holding it up against the theory that measurable quantities of some metal are not always found in solution.

The second point in which Whitney's formulation has been confusing to some of his successors is that he did not lay sufficient stress on over-voltage. Since the solution pressure of iron is higher than that of hydrogen even in presence of practically pure water, iron should corrode in pure water as indeed it does. In regard to this, Whitney[3] says: "Iron dissolves in pure water qualitatively just as in a solution of copper sulphate, hydrogen being deposited in place of copper. The velocity with which this process proceeds will depend on the temperature and on the hydrogen-ion concentration in the water. When this concentration is so great that the potential difference exceeds a certain value, the hydrogen will be evolved as gas, separating from the liquid at the surface of the iron as bubbles. This potential value depends on the state of the surface so that it is usually higher than the theoretical value for polarization by hydrogen when the gas is in equilibrium with the solution.

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[1] Z. physik. Chem. 4, 152 (1889).

[2] LeBlanc: "A Text-Book of Electrochemistry," 177 (1907).

[3] J. Am. Chem. Soc. 25, 399 (1903).

Below this value, the hydrogen, which is nevertheless being deposited upon the iron, but at a concentration below that corresponding to atmospheric pressure, slowly dissolves in the water, forming an ordinary solution of it, and escapes by diffusion."

There is a reference to over-voltage here; but it is not very clear-cut and it has been misunderstood repeatedly. Nowadays, we know that hydrogen over-voltage is due to polarization by electrically-neutral, monatomic hydrogen[1] and hydrogen will be given off as gas or be dissolved by the solution only as the infinitely small amounts of monatomic hydrogen, presumably adsorbed on the surface, react to form molecular hydrogen.

This is a very different thing from the hypothesis postulated by Bengough and Stuart[2] and absolutely nullifies their criticism. "On the electrochemical view, the conclusion would be that a minute trace of hydrogen would adhere to the metal for long periods of time, entirely preventing corrosion in absence of oxygen. Yet when metal is attacked by very dilute acids (*e.g.* zinc in 1:5000 acetic acid), the attack proceeds steadily in spite of the evolution of hydrogen, visible under the microscope, at many points over the metal. It seems clear, therefore, that a hydrogen film is not a good, or even a moderate, protective against corrosion." They have forgotten all about polarization and are merely considering the ohmic resistance of a film of gas.

Whitney[3] says that "there is no doubt that iron, even at ordinary temperatures reacts with pure water, in accord with this conception. The experiments on this point, carried out by Deville at high temperatures only, showed a balanced condition at various temperatures for the reaction.

$$3\ Fe + 4\ H_2O = Fe_3O_4 + 4H_2.$$

He found experimentally that water vapor in contact with iron must produce a certain concentration of hydrogen gas to be in equilibrium; in other words, if the hydrogen was continually removed, the iron could continually oxidize. Within the range of temperature employed (200° to 1000°C), he found that the pressure of the hydrogen produced by the action between iron and water increased as the pressure of the water vapor was increased. As the temperature rose, the hydrogen concentration (or pressure) at equilibrium diminished; in other words, the lower the temperature in his experiments, the greater the tendency for oxidation of the iron. According to these results we should expect water to act on iron to generate hydrogen even at ordinary temperatures, and it is a well-known fact that very finely divided iron such as is obtained by dry reduction of iron salts, reacts with pure water and generates hydrogen.

"This fact, that pure water causes solution of iron, is in accord with other experimentally discovered facts. Mr. G. O. Adams, in connection with a thesis presented to this institute in 1900, made analyses of various samples of

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[1] Ostwald: Z. Elektrochem. **6**, 40 (1889); Müller: Z. anorg. Chem. **26**, 11 (1901); Tafel: Z. physik. Chem. **34**, 200 (1900); **50**, 641, 713 (1905); Lewis and Jackson: Proc. Am. Acad. Arts Sci. **41**, 399; Z. physik. Chem. **56**, 207; Brunner: 331 (1906); Bennett and Thompson: J. Phys. Chem. **20**, 296; Bancroft: 396 (1916); Aten: Proc. Acad. Sci. Amsterdam, **18**, 1379 (1916).

[2] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, **28**, 88 (1922).

[3] J. Am. Chem. Soc. **25**, 396 (1903).

gases collected from radiators in different houses where the hot-water gravity heating system is used, and where different water supplies are concerned, and always found a large quantity of hydrogen gas. In most cases, on opening the air-cock of the radiators the gas could be lighted with a match. A number of such mixtures were analyzed. These varied in composition, but were mainly mixtures of nitrogen and hydrogen with usually no oxygen. The hydrogen content varied from 44 to 78 percent by volume. Measurable quantities of carbon dioxide or of hydrocarbons were not usually present."

The results of Mr. Adams have been confirmed in recent years by Mr. Speller of the National Tube Company. Bengough and Stuart[1] believe that when zinc corrodes in pure distilled water, no evolution of hydrogen can be observed although considerable local corrosion (type B) takes place. "This is in sharp contrast with the behaviour of zinc in very dilute acid, where the evolution of hydrogen is quantitative. . . . The first observation, *i.e.* that no hydrogen is involved in the local corrosion of zinc, is of great importance in connection with theories of corrosion; and further observations have shown that no hydrogen appears when many other metals undergo corrosion in distilled water—in fact, it is only in the case of highly electro-positive metals (*e.g.* calcium) that hydrogen gas appears during local corrosion. Yet the electro-chemical theory assumes that the first action in such corrosion is the passage of metal *ions* into solution, and the displacement of hydrogen in the case of all metals. The assumption really is that all corrosion by water and salt solutions is of the acid type.

"There is, however, no direct evidence for this assumption, but some against it. Lambert and Cullis[2] found no trace of lead in pure water which had been in contact with pure lead in a vacuum for several months. On the electro-chemical theory, which states that corrosion is due to electrical currents set up between portions of the metal of different potentials, Lambert explains the above result by assuming polarization of the areas of low potential by displaced hydrogen, which stopped corrosion so rapidly and completely that neither metal nor the hydrogen responsible for the stoppage could be detected. A similar explanation would doubtless be applied to the fact, observed by many investigators, that local corrosion (type B) even of ordinary commercial metals never takes place in absence of oxygen. Thus Friend detected very little change in Swedish iron kept for twelve years in pure water in absence of air."[3]

This is not helpful at all because we come out with the same analytical result whether we postulate that oxygen acts as a depolarizer or reacts direct with the metal. Consequently experiments of this sort are distinctly a waste of time. It is probable that with Friend's Swedish iron he had either an especially high over-voltage, or the formation of an adherent film of ferrous oxide. Whitney[4] obtained quite different results with other samples of iron

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[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 87, 88 (1922).

[2] Lambert and Cullis: J. Chem. Soc. 107, 214 (1915).

[3] Carnegie Scholarship Memoirs, 1922, 125.

[4] J. Am. Chem. Soc. 25, 398 (1903).

in some experiments which he made for another purpose. "To learn whether carbonic acid was necessary to iron-rusting, a clean bottle was steamed out for a time to remove soluble alkali from the glass and was then filled with pure distilled water which was kept boiling by passing steam through it for fifteen minutes. While still boiling, a bright piece of iron was placed in the bottle. A stopper (in some cases rubber and in others cork) carrying a tube open in a capillary several inches above the stopper, was inserted into the bottle and firmly fastened in place, the water being kept boiling. Finally, the glass capillary was heated hot by means of a blowpipe and sealed by squeezing the walls together. The bottle was then allowed to cool to a temperature of about 80° C; and the neck of the bottle was finally covered with paraffin to prevent leaking. It was thought that in this way the oxygen, carbonic acid, and other gases in the water were completely removed. Bottles containing iron and sealed in this manner have stood without any visible change for weeks. In some cases a little air was subsequently admitted to bottles which had stood in this way with the iron apparently unaffected, and within a few minutes the water became cloudy and assumed a yellow color. Ordinary rust rapidly deposited upon the glass and in spots upon the metal. In fifteen or twenty minutes the production of rust throughout the bottle was perfectly evident. It seemed plain from the rapidity of formation of oxide and its precipitation on the glass, that the iron had dissolved in the water before the addition of the air, and that the latter simply permitted the formation of the insoluble oxide.

"Mr. J. A. Collins, in connection with his thesis of 1898, performed a similar experiment which shows that the iron is dissolved in the water and that its appearance as rust is a secondary phenomenon due to the action of oxygen on the solution. A cleaned iron pipe 0.5 inch by 15 inches, sealed at one end and having a screw cap to fit the other, was filled with boiling distilled water, and the boiling continued by heating the pipe until half the water had boiled away. While still rapidly distilling, the cap was screwed on tightly and the tube heated to about 125°C for an hour. On cooling and removing the water from the pipe, it was found to be perfectly clear and colorless, but, on exposure to air in a glass vessel, it rapidly precipitated rust. The pure water had dissolved iron in some form from the clean metallic surface, and this remained in solution until precipitated by the oxygen of the air. In experiments with air-free water in contact with iron, in glass bottles and flasks, Mr. Collins let into the flasks containing only the pure water together with its vapor and the bright iron, air which had been freed from carbonic acid by being exposed to the action of a barium solution in a closed bottle for twelve hours, the bottle being repeatedly shaken to hasten the absorption. In case of this treated air, the production of rust in the flasks was evidently as rapid as with ordinary air.

"A similar experiment with purified oxygen gave the same result. One is forced to conclude from such results that if the rusting is due in any way to carbonic acid it is rapidly brought about by such a quantity of this gas as is left in air or oxygen after treatment with a barium hydroxide solution; in other words, by an inappreciably small quantity. As this acid could owe its activity solely to its hydrogen ions, because of the fact that the carbonate ion has no rusting or dissolving action on the iron, it is interesting to note that in the case of recently boiled water, the hydrogen-ion content due to carbonic acid may well be as low as the hydrogen-ion content due to the dissociation of pure water."

Dunstan, Jowett and Goulding[1] have questioned Whitney's statements of fact. "An attempt has been made by Whitney[2] to apply the theory of electrolytic dissociation to the explanation of the rusting of iron. Water being assumed to be slightly dissociated into hydrogen and hydroxyl ions, it should be capable of dissolving minute quantities of metallic iron, owing to the formation of an electric circuit containing iron as the positive and hydrogen as the negative element. If this is the case, the rusting process would be explained, the ferrous hydroxide first formed absorbing oxygen from the air. Substances such as alkaline salts interfere with, or altogether prevent, rusting by hindering the accumulation of hydrogen ions, whilst acids and certain salts tend to accelerate rusting by increasing the accumulation of hydrogen ions. When the concentration of the hydrogen has attained a certain maximum, the hydrogen, according to Whitney, is evolved as a gas. This is, however, contrary to fact, no hydrogen being liberated in ordinary circumstances during the rusting of iron. Careful experiment has also failed to confirm Whitney's statement that iron dissolves to a slight extent in water, whilst the theory in question is shown to afford no explanation of the fact, established during the course of this investigation, that substances other than alkaline salts, such as chromic acid and potassium dichromate, prevent the rusting of iron."

"It has been assumed by Whitney (loc. cit.) that water, on the electrolytic hypothesis, being slightly dissociated, is capable of dissolving iron in the absence of oxygen or of carbon dioxide owing to the formation of a voltaic couple in which the iron acts as the positive element, whilst the negative element consists of the few hydrogen ions which the water normally contains. On this supposition he has founded a theory of rusting. He shows that theoretically those substances, such as acids, which permit of the concentration of hydrogen ions accelerate rusting, whilst those substances, such as alkalis, which diminish the concentration of the hydrogen ions inhibit rusting. The experimental evidence adduced by Whitney in support of the fundamental assumption that iron dissolves appreciably in pure water in the absence of oxygen or carbonic acid is slender and unsatisfactory. The theory also involves the assumption that hydrogen is liberated during the rusting of iron, but no evidence of the formation of free hydrogen is produced by Whitney, and we have never noticed its production in any of the experiments we have conducted. As regards the solubility of iron in water, Whitney describes an experiment in which a piece of bright iron was placed in a bottle of boiling water, and, while the water was still boiling, a stopper carrying a glass tube was firmly inserted in the neck of the bottle and the end of the glass tube

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[1] J. Chem. Soc. 87, 1551 (1905).
[2] J. Am. Chem. Soc. 25, 394 (1903).

sealed in the blowpipe; the stopper and the neck of the bottle were afterwards coated with paraffin wax. In experiments thus made, he states that the iron remained without change for weeks, but, on admitting air, rust was formed in a few minutes, the water becoming cloudy and assuming a yellow colour. In 15 or 20 minutes, rust was produced throughout the bottle, being deposited on the glass as well as on the metal. From these results, Whitney concludes that the iron had dissolved in the water before the admission of air, and that the oxygen admitted reacted with the dissolved iron with the formation of rust.

"We have repeated this experiment in the following manner. A flask of 600 cc capacity, filled with distilled water, was boiled for 15 minutes; two pieces of purified iron each about 1-1/2 inches square were then placed in the flask, and an india-rubber stopper carrying a glass tube which projected 7-8 inches above the stopper and ended in a capillary was fitted into the neck of the flask, the water being kept boiling continuously. The water was allowed to boil for five minutes longer, when the capillary was sealed and the stopper coated with paraffin wax. This flask was left at the ordinary temperature for three weeks, in the course of which no visible change occurred. It was then opened, when one-half of the liquid was quickly poured into a beaker, the other half being left in contact with the iron in the flask. The liquid in the beaker on exposure to the air showed no cloudiness, no yellow coloration, and no separation of rust. In fact, on testing the liquid for iron by the extremely delicate thiocyanate reaction not a trace could be detected. The pieces of iron in the open flask after an hour showed signs of rusting, just as in ordinary cases, but the phenomena described by Whitney were not observed. We are therefore unable to confirm Whitney's statement that liquid water alone is capable of dissolving even an infinitesimal quantity of iron. This being the case, the theory based on this statement becomes untenable.

"It having been proved that iron rusts in the presence of oxygen and water without the aid of carbon dioxide, it follows that the inhibitive action of alkalis on the process of rusting must find some other explanation than that hitherto accepted, which assumes that alkalis remove carbon dioxide, in the absence of which rusting cannot occur."

The whole difficulty is in the tacit assumption that iron is iron and that the sample used by Whitney behaved exactly like the sample used by Dunstan. If Whitney used a somewhat impure iron, as he undoubtedly did, the impurities might well have caused such a decrease in the over-voltage that a perceptible amount of corrosion took place and a perceptible amount of hydrogen was set free in the one case, whereas that did not happen with Dunstan's samples of iron. It must be borne in mind that the theory only calls for the actual corrosion of iron and the setting free of hydrogen in so far as the over-voltage does not interfere. Under favorable conditions, the actual corrosion may be very small and may well be negligible in an experiment lasting only three weeks.

As I shall take up later the question of the action of alkalies and bichromates in inhibiting rusting, we need not worry for the present over Dunstan's assumption that the electrolytic theory of corrosion cannot account for these phenomena.

In later paragraphs Whitney[1] pointed out that carbonic acid may act as a carrier under certain conditions. "Free alkali added to a boiler of water not only greatly reduces the concentration of the hydrogen ions, from whatever source, thus diminishing the electrochemical reaction of interchange between hydrogen and iron and in the boiler itself, but also produces another valuable effect. If a steam or hot-water heating system is fed with a water which is not naturally alkaline, a part at least of the carbonic acid, which it always contains, will be driven from the water on boiling and pass to the cooler portion of the system to be redissolved in condensing water. Thus the return pipes of the system will be subjected to the action of this acid or hydrogen-ion solution. No protecting scale of salts from the water being produced in these return pipes, such as is almost always produced in the boiler itself, the corrosive action will be most marked in the return pipes, and especially where the pipes are exposed to the action of continuous supplies of the water in motion. This will prevent the establishment of equilibria and the iron will be continually removed. It ought also to be removed according to the previous discussion, though more slowly, even if no carbonic acid or other acid were present, because of the hydrogen ions of the pure water. This reaction could again be reduced by the presence of volatile alkali in the condensed water, but in practice this latter is usually a negligible effect compared with the effect of volatile acid.

"I wish now to show that the effect of the carbonic acid is actually a cyclic one, the same molecule of acid doing unlimited corrosive work, and that the very harmful corrosion of return pipes in many heating systems may be directly attributed to this usually inconsiderable and unnoticed ingredient of the water. To make this point clear, let us imagine a steam-heating system made up of a boiler, with steam pipes leading to various heating stacks and radiators from which return pipes bring the condensed steam back to the boiler below the water-level. For simplicity, we assume that the plant is run without the addition of water after the boiler has been originally charged. In other words, no steam is blown out into the air and the plant is not used, as some are, to incidentally supply hot water for foreign uses, which thus requires a continual water feed. Our closed system usually contains, when in actual running condition, a number of dead-ends where gases have accumulated and where the pipes are cold. This may be observed in many radiators of common type. Into this colder portion of the system, the gases such as oxygen, nitrogen, and carbonic acid, which were originally in the feed water, will collect. Here they will dissolve in the condensed water which is to return to the boiler, the carbonic acid being especially soluble. The carbonic acid or its active hydrogen will cause the solution of iron from the return pipes and this iron will be carried back towards the boiler as bicarbonate of iron, being held in solution just as is

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[1] J. Am. Chem. Soc. 25, 401 (1903).

calcium carbonate in water containing carbonic acid. This may be represented by the reaction

$$Fe + 2CO_2 + 2H_2O = H_2Fe(CO_3)_2 + H_2.$$

"In the case of the bicarbonate of calcium solution, it is well known that boiling decomposes the salt and liberates half of the carbonic acid, leaving a precipitate of calcium carbonate. In case of the soluble bicarbonate of iron, as will be shown later, the decomposition of the compound by heat, liberates all of the carbonic acid instead of half of it and produces the insoluble oxide or hydroxide of iron. Whether this decomposition of the soluble iron salt takes place in the boiler after the solution has returned to it, or in the return pipe where the proximity to the boiler produces a sufficiently high temperature, is of no immediate importance. In either case, the carbonic acid is all set free and must immediately return with steam to the cooler parts of the system; there again it will dissolve in the condensate, again render soluble some iron and carry it towards the boiler and so forth. In each cycle of this kind hydrogen will be set free which will remain in the cooler parts of the system, as it is but slightly soluble in water. It seems necessary, therefore, that in common practice a very small quantity of carbonic acid must often cause an unlimited amount of corrosion, without in any way losing its power to continue the process. The process of corrosion of the iron in this case will amount *in toto* to the union of iron with the oxygen of water and liberation of hydrogen, the carbonic acid acting merely as a catalyzer, where the mechanics of its action is apparent. This peculiar condition of affairs has been observed by us in certain large heating systems where we have found, first the carbonic acid of the feed water; secondly, much carbonic acid mixed with hydrogen, nitrogen, and oxygen in dead-ends or cold parts of the system; thirdly, water in the return pipes, where very rapid corrosion of the piping was taking place, in which much dissolved bicarbonate of iron was found; and finally, much precipitated oxide of iron in the boiler and hottest parts of the return pipes.

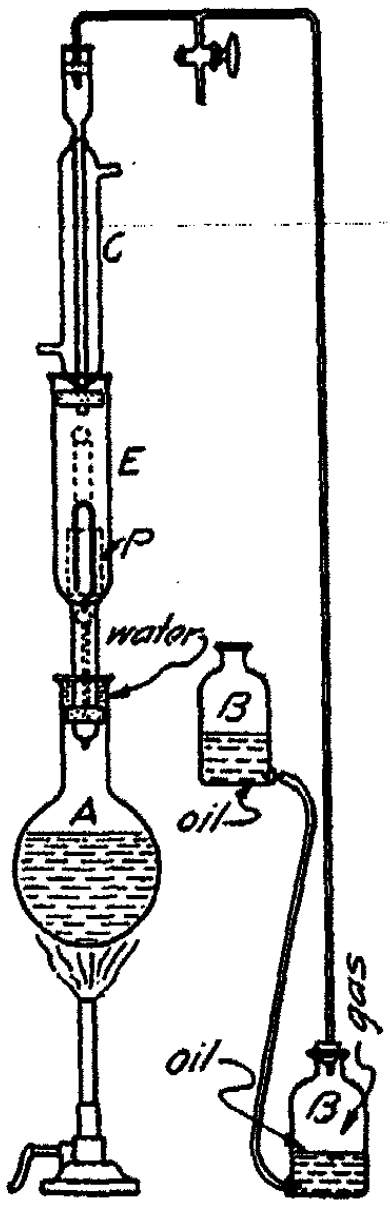

Fig. I

"It has been possible also to reproduce these phenomena in the laboratory in various ways and in some cases in glass apparatus where the complete cycle becomes practically visible. In connection with his thesis, Mr. C. L. Wright arranged an apparatus of which a sketch is shown. Pure distilled water was boiled in the flask A, and various quantities of air and carbonic acid mixtures were enclosed in the system which was kept nearly at atmospheric pressure by the liquid seal made by the bottles B connected with the condenser C. The steam condensed and took up a little of the carbonic acid; this solution came into contact with a piece of cleaned pipe, P, from which the outer layer had been removed in the lathe. This iron was supported in an extractor, E, between the condenser and the boiler in such a way that it was alternately covered with the water and uncovered by the intermittent siphon action of the extractor.

"In the first few experiments a precipitate was soon formed in the boiler which was not analyzed, but which was evidently a mixture of hydroxide of iron and silica from the glass. Subsequent experiments in the same apparatus differed in result from the first one and showed that, in the absence of free oxygen, the boiler water simply became black and opaque but showed little or no precipitate. The glass tube leading from the condenser to the boiler was also quickly coated with a black deposit of iron oxide. It was evident that iron was being dissolved and the resulting compound decomposed in the boiler, and in the hot return tube, but it was at first thought peculiar that the precipitate which appears when the glass or flask is a new one, was not produced in subsequent experiments, with the same apparatus. This led to attributing the actual formation of a precipitate in the first case to the presence of dissolved glass. The dark color could only be due to the iron. The clear, black, filterable solution obtained from such previously-used apparatus was then shown to be a colloidal solution of iron oxide by the following method: Small quantities of such salts as sodium and barium chloride were added to portions of the clear, black water, and they caused an immediate coagulation and a consequent heavy precipitate, coupled with complete decolorization of the solution. This precipitate, well washed by decantation with pure water, was treated with dilute sulphuric acid in a closed vessel and pure air passed through this and then through a vessel containing a barium hydroxide solution. The failure to produce a precipitate of barium carbonate in this barium hydroxide solution showed that the original compound did not contain a carbonate. The precipitate was shown to contain iron by dissolving it in acid, oxidizing and precipitating the ferric hydroxide by ammonia. The formation of this colloidal solution of ferrous oxide is in exact accord with the principles which determine the formation of colloidal solutions in general. It is a general principle that whenever any substance which is by nature insoluble, is formed in water, it will tend to remain in a colloidal or suspended state until coagulated by electrolytes.

"In the production of most precipitates in common laboratory reactions, there are always sufficient electrolytes present to account for the coagulation of the insoluble substances, if we may judge by the concentration usually necessary where measurements have been made. Where this is not the case, a colloidal state usually results. In the case at hand, there are practically no electrolytes present when the soluble ferrous bicarbonate is decomposed by heat, as this process requires the presence of but exceedingly small quantities of soluble salts in the solution at any one time. The insoluble ferrous oxide consequently remains in the colloidal state. This colloid may be precipitated by salts dissolved from the glass vessel, if of sufficient concentration, as was the case with new glass apparatus, and in this respect this colloid is like many others, such as platinum and silica.

"The ease with which the soluble iron salt is decomposed by heat was well shown in the glass tube connecting the condenser and boiler, the return pipe of the above experiment. Above the stopper of the flask, where this tube was fairly cool, the glass remained clear, but below the stopper where the tube was heated by the steam of the flask, it was covered deeply with a black deposit, probably ferrous oxide. The deposition of this substance at this part of the return tube, commenced almost immediately on starting the experiment.

"An experiment carried out in this way where pure water and carbon dioxide were used, where analysis showed the gaseous mixture to contain eleven percent carbon dioxide, produced such rapid corrosion of the iron that within a few days nearly a third of the exposed surface had been eaten away to depths of several hundredths of an inch, at which rate an ordinary pipe would not last more than a few months. It is not surprising that carbonic acid should dissolve iron under these conditions, but the fact that this corrosive action is a cyclic one, in which under suitable circumstances even a trace of carbonic acid may dissolve an unlimited quantitiy of iron without losing its corrosive power, has not received sufficient attention."

Whitney[1] was quite clear as to the effect of scale, though it is quite possible that he did not emphasize this factor as much as seems desirable twenty years later. The polarization by hydrogen "should greatly limit the velocity of solution of the iron, even if there is no other complicating effect due to the production of an insoluble compound, an oxide or hydroxide, in case air be present. This is usually the case in practice. The production of a compact adherent coating of oxide on the surface of the iron generally retards the corrosive action. Especially is this true at temperatures of steam where the magnetic oxide is formed. This oxide always forms as an adherent solid coating on the iron and seems to be interrupted only by cracks caused by its unequal coefficient of expansion compared with the iron. The red oxide or rust is always flocculent and spongy and, besides not protecting the iron, actually seems to increase the velocity of corrosion in its vicinity. It is common to attribute to the red oxide or rust a catalyzing effect on the corrosion of iron."

That Whitney's attitude in regard to films was inadequate is shown in the next paragraph.[2] "If the primary rate of corrosion of iron, independent of subsequent formation of insoluble substances, is simply dependent upon the concentration of the hydrogen ions of the water, anything which reduced this concentration should also reduce the corrosion. . . . This reduction of the hydrogen ion concentration may be brought about by the addition of any alkali to the water. That the corrosion is thereby diminished is a well-known fact and one that already receives many practical applications. Iron and steel tools in process of manufacture, between the roughly ground state and the final polished condition, are often kept under water saturated with lime. This prevents the rusting which would quickly take place if they were left in moist air. The effect of the lime must be attributed solely to the hydroxyl ions which in turn reduce the concentration of the hydrogen ions of the water.

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[1] J. Am. Chem. Soc. 25, 400 (1903).

[2] Whitney: J. Am. Chem. Soc. 25, 400 (1903).

Neutral salts of calcium do not exert this effect and hence it can not be attributed to the calcium compound nor to the calcium ion. Other soluble alkalies do it equally well and these contain, in common, only the hydroxyl ion."

It would be a bold man nowadays who would question the formation of a surface film on iron in alkaline solutions and consequently the effect of the lime cannot be due solely to the reduction of the concentration of the hydrogen ions of the water in the sense that Whitney means. Whitney was right as far as he went and it is quite possible that he went as far as was wise twenty years ago.

As Whitney was discussing the corrosion of iron, it was not necessary for him to consider the corrosion of sodium by water, especially as this case had been discussed explicitly by Nernst.[1] "Let zinc be brought in contact with acids, or sodium with water: then the electrostatic charge is obviously great enough to drive the positive hydrogen ions out of the solution and into the metal in which they dissolve; the hydrogen is able to separate from the metal in an electrically neutral form as soon as its concentration in the metal shall have reached a sufficient amount, *i.e.* as soon as its vapor pressure shall amount to the pressure of one atmosphere."

There is nothing in this paragraph or in Whitney's paper to the effect that a pure metal cannot corrode and yet Bengough and Stuart[2] say that the characteristic conception of the electrolytic theory of corrosion "is that of a non-uniform distribution of anodic and cathodic areas over the surface of the metal, such areas being caused by local differences in solution pressure . . . . An ideally pure and homogeneous metal is assumed to be incorrodible." I think that every chemist would expect a pure and theoretically uniform sheet of sodium to be attacked by water, though he could not, on that statement of facts, predict at what point the first bubble of hydrogen would appear. Similarly he would admit that copper would be corroded by concentrated nitric acid containing nitrous acid regardless of how pure or how uniform the metal was.

Fifteen years ago Walker[3] said that "every metal, when placed in water or under such conditions that a film of water may condense upon it, tends to dissolve in the water, or, in other words, to pass from its atomic or metallic condition into its ionic condition. This escaping tendency of the metals varies from that shown by sodium or potassium, which is so great as to cause instant and rapid decomposition of the metal and water, to gold or platinum where such tendency is zero. Between these two extremes we find the other common metals, including thereunder the element hydrogen, which may be considered as a metal."

It is quite true that Messrs. Bengough and Stuart could justify their statement by quotations; but their attitude should not be that of special pleaders trying to make a point.

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[1] "Theoretical Chemistry," 612 (1895).

[2] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 54 (1922).

[3] J. Iron Steel Inst. 1, 70 (1909).

In 1906 I pointed out[1] that "the most striking characteristic of an electrolytic reaction is that it occurs in two places—at the anode and the cathode. This peculiarity can be made less marked by bringing the electrodes nearer and nearer together. When the distance between them vanishes we have a chemical reaction in the ordinary sense of the word and not an electrochemical reaction. Any chemical reaction therefore which can be made to take place electrolytically must consist of an anode and a cathode process.[2] Considering the matter in this light we see that in the chemical reaction there is a possibility of the anode and cathode processes interfering, and of one perhaps masking the other.

"In some cases it is easy enough to tell what the anode and the cathode processes are. If we dissolve zinc in sulphuric acid, the formation of zinc sulphate is the anode process and the evolution of hydrogen is the cathode process. Now we know that pure zinc does not dissolve readily in sulphuric acid. Consequently we should expect to find a difficulty of some sort if we electrolyze sulphuric acid between zinc electrodes. We find this in the form of the so-called 'excess voltage' at the cathode; and in the electrolytic process we can obtain a more or less quantitative measurement of the phenomenon though we are still far from knowing the cause of it.

A less simple case is that of copper in dilute nitric acid. Copper reacts chemically with dilute nitric acid, setting free nitric oxide. The formation of copper nitrate must be the anode process and the reduction of the nitric acid the cathode process. When we start to test this we find difficulties. Everybody knows that we get ammonia instead of nitric oxide if we electrolyze dilute nitric acid, using a copper cathode. We have here an apparent contradiction, the chemical reduction yielding nitric oxide and the electrochemical one ammonia. Mr. Turrentine was good enough to solve the mystery for me. When copper reacts chemically with nitric acid, the anode product, copper nitrate, is formed at the same spot that the reduction takes place. In the electrolytic reduction of nitric acid with a copper cathode, the reduction takes place in a solution practically free from copper salt. The conditions are therefore not the same in the two cases. Mr. Turrentine therefore electrolyzed a solution of nitric acid and copper nitrate using a copper cathode. A gas was evolved at the cathode which proved on analysis to be chiefly nitric oxide. This experiment can be done in another form which is more striking. If dilute nitric acid be electrolyzed between copper electrodes, there will at first be no evolution of gas at the cathode. Gas will begin to appear as soon as the blue solution formed at the anode comes in contact with the cathode. A corollary to this is that ammonia would be formed in the chemical reaction between copper and nitric acid if the concentration of the copper salt could be kept sufficiently low. There did not seem to be any salt which one could add to the solution without introducing more complications than were eliminated. The difficulty was overcome by Mr. Turrentine in a distinctly ingenious manner. Strips of copper were hung vertically in a tall vessel. The copper nitrate

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[1] Bancroft: Trans. Am. Electrochem. Soc. 9, 13 (1906).

[2] Cf. Traube: Ber. 26, 1473 (1893); Haber: Z. physik. Chem. 34, 514 (1900).

flowed to the bottom of the vessel and the copper was removed by electrolytic precipitation in the form of cupric hydroxide. No current flowed through the copper strips and there was no copper cathode; but ammonia was formed.

"These experiments were performed to prove that the difference between the electrochemical and the chemical corrosion of copper by nitric acid was an apparent one only and due to an unsuspected difference in the conditions. In addition they illustrate the superior flexibility of the electrochemical method over the chemical method. In the electrochemical method there is no difficulty in varying the concentration of the copper salt at the cathode between any desired limits, while this is very difficult to do in the case of the chemical method. This is in addition to the advantage, which the electrochemical method always has, of permitting a wide variation in the rate of reaction for constant temperature and constant concentration. If we are ever to have a thorough knowledge of the chemical reactions between nitric acid and the metals we must study the problem electrochemically.

"When metals are acted on slowly by oxygen in presence of moisture, it is known that half the oxygen reacts with water to form hydrogen peroxide, this hydrogen peroxide then often reacting with the metal. By shaking a zinc amalgam with a solution containing sodium and calcium hydroxides, Traube[1] was able to isolate the insoluble calcium peroxide. So far as we now know hydrogen peroxide is formed at the anode only under special conditions, such as electrolysis of a concentrated sulphuric acid with a high anode density. Even under these conditions it is by no means certain that hydrogen peroxide is not a secondary product resulting from the decomposition of persulphuric acid. On the other hand hydrogen peroxide is the first reduction product at an oxygen cathode. In the reaction studied by Traube the oxidation of the zinc is the anode process and the formation of hydrogen peroxide is the cathode process. A consequence of this is that if we electrolyze a caustic soda solution between zinc electrodes and bubble in air round the cathode, we ought to get a corrosion at the cathode due to the secondary reaction of the hydrogen peroxide with the zinc cathode. It has been found that the cathode does corrode under these circumstances; but it is a little difficult to tell whether this corrosion is due to hydrogen peroxide or to the oxygen of the air. With an iron cathode the corrosion has never been anything like as great as was obtained by simply bubbling air against the plate when no current was passing. This whole question calls for much more study than has yet been given to it.

"The slow oxidation of metals in contact with solutions means the corrosion of these metals by these solutions, a very important problem. If we can substitute electrochemical methods for chemical ones, it means an enormous saving in time and a corresponding increase in the number and in the quality of the data which we can accumulate. A single experiment on chemical corrosion may easily last six weeks. This means great difficulty in keeping conditions constant. By the time that experiment has been repeated several times with the variations which each repetition suggests, six months or a year have passed. On the other hand an experiment in electrolytic corrosion can

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[1] Ber. 26, 1471 (1893).

be run through in a few hours, seven or eight at the outside. The advantage is obvious provided the results are the same in the two cases. We can see in a moment that the two phenomena must usually be the same. Suppose we have a copper plate[1] in a sulphate solution which contains dissolved oxygen and suppose that the concentration of oxygen is not the same over the entire surface of the plate. We shall then have an oxygen concentration cell with copper electrodes and a current will tend to flow through the solution from the place of lower oxygen concentration to the place of higher oxygen concentration. Since the dissolved oxygen will never be absolutely uniform in concentration, its effect will always be to start a miniature electrolytic cell. The only real difference between the chemical corrosion and the electrolytic corrosion will be in the magnitude of the current. A special case occurs when the current makes a metal anode passive. In that case the metal does not corrode in that solution. Iron becomes practically passive when made anode in caustic soda solution or in concentrated nitric acid, and iron does not rust to any appreciable extent in these solutions. An iron anode is not attacked in a carbonate solution and is attacked in a bicarbonate solution. Iron does not rust readily in the first solution and does in the second. Iron dissolves quantitatively as anode in sulphate or chloride solutions and rusts with surprising rapidity in these solutions. Nickel becomes passive in sulphate solutions and does not rust. Nickel does not become passive in sodium chloride solutions and it corrodes in these solutions, though not rapidly. In general we may say that any addition which makes a metal passive in any solution will prevent the metal from corroding in that solution.

"You have been told today that electrolytic corrosion and chemical corrosion are two fundamentally different things.[2] I should prefer to word that somewhat differently and I should say that electrolytic and chemical corrosion are fundamentally one and the same. Any apparent differences will be found to be due to special differences in the conditions, as in the case of copper and nitric acid to which I have already referred. It may also happen that an insoluble salt will be formed as an adherent crust in one case and as a non-adherent powder in another. This will of course have a material effect on the rate of corrosion whether electrolytic or chemical; but such cases are perfectly simple if examined carefully. One apparent discrepancy has occurred in our own work. When pure manganese is made anode in caustic soda solution, permanganate is formed. A caustic soda solution reacts with metallic manganese chemically, forming a hydroxide of manganese and setting free hydrogen. Mr. White soon found that a manganese anode forms permanganate in caustic soda solution only when the anode current density exceeded a certain limiting value. With lower current densities manganous hydroxide or manganese dioxide is formed. The apparent discrepancy is therefore an imaginary one due to the artificial difference in the rate of corrosion.

"We can now pass to the question of the corrosion of alloys, under which heading the corrosion of iron could have been taken up. Very little careful

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[1] Cf. Haber: Z. Elektrochem. 12, 32 (1906).

[2] Toch: Trans. Am. Electrochem. Soc. 9, (1906).

work has been done on the electrolytic corrosion of alloys and the accepted theory of the phenomena is not at all in accord with the facts. In one of the latest text-books on electrochemistry we read[1] 'that obviously the potential of a mixture of two metals determines its behavior as anode.' This means that the less noble metal or the less noble phase will dissolve first. In the case of copper-tin alloys annealed just above 200°, we have five possible solid phases. From 100 to 87 percent copper we have a series of solid solutions known as the α-crystals. From 74.5 to 67 percent we have the homogeneous δ-crystals, also a series of solid solutions. These are the crystals which Heycock and Neville believed to be the compound Cu_4Sn. At 61.3 percent copper we have the compound Cu_3Sn, the only compound in the series. From 41 to 40 percent we have a new series of solid solutions, the ε-crystals, formerly supposed to be CuSn. Lastly, we have pure tin. The experiments of Herschkowitsch[2] and unpublished work by Shepherd show that the ε-crystals have a potential differing from that of pure tin by only a few millivolts, while the Cu_3Sn, δ, and α-crystals differ in potential from pure copper by an even smaller amount. The order of solubility should therefore be tin, ε, Cu_3Sn, δ and α, the last being the least readily corroded. As a matter of fact, in most solutions tin and the α-crystals are the most readily attacked, while the ε-crystals are the least readily corroded.[3]

"The cause for this discrepancy between theory and experiment is that we are reasoning from static to dynamic experiments, from a stationary state to a changing one. An electromotive force is measured on open circuit with no current flowing. Electrolytic corrosion takes place on closed circuit with a current flowing.

"Reasoning from electromotive force measurements to current phenomena is permissible only when no surface change takes place and when equilibrium conditions are satisfied. We know now that neither of these conditions is satisfied with the bronzes, and there is no reason for supposing that these conditions will be fulfilled except in special cases. A number of the bronzes become passive owing to the formation of a surface film of stannic oxide. In both the copper-rich bronzes and the copper-rich brasses, the reaction between the alloy and a copper sulphate solution is so very slow that no reversible equilibrium is reached during corrosion.

"While we cannot predict the actual way in which an alloy will corrode, from electromotive force measurements of the phases, we can predict that any change in the current efficiency with a given alloy as anode will coincide more or less closely with the appearance or disappearance of a phase. Some experiments on the behavior of bronzes by Mr. Curry bring this point out very clearly. In sodium sulphate solutions the only phases to dissolve are pure tin and the copper-rich crystals known as the α-crystals. The current efficiency decreases as the percentage of these two sets of crystals decrease and is practically zero for the δ, Cu_3Sn, and ε-crystals. In sodium acetate solutions we

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[1] Foerster: "Elektrochemie wässeriger Lösungen," 208.

[2] Z. physik. Chem. 27, 123 (1898).

[3] [The argument does not depend at all on the assumptions made as to the nature of the solid phases. W. D. B.]

have a similar behavior, but the α-crystals are much less readily corroded in the sulphate solutions and the current efficiency becomes practically zero as soon as any δ-crystals are present. In sodium nitrate solutions the δ-crystals corrode until the copper content has fallen to about one-half the maximum. There is practically no corrosion with the tin-rich δ crystals, with Cu_3Sn, and with the ε-crystals, while alloys containing free tin corrode readily. In acidified ammonium oxalate solution, α and δ-crystals dissolve with one hundred percent current efficiency, while Cu_3Sn is less readily attacked and the current efficiency drops to about twenty-five percent. Still other relations are found in alkaline sodium tartrate solutions, while with sodium chloride solutions there is no tendency for the alloys to become passive and the current efficiency is approximately one hundred percent over the whole range from pure copper to pure tin.

"We thus see that the electrolytic corrosion varies with the nature of the solution and that the changes in the current efficiency stand in a clearly-marked relation to the changes in the nature of the crystals present in the solid alloy. Special experiments on the chemical corrosion of the bronzes in persulphate and in chloride solutions show that the results are identical with those obtained for electrolytic corrosion in sulphate and in chloride solutions respectively. Since the identity of the chemical and the electrolytic corrosions has been proved for these two typical solutions, it is fair to assume that a corresponding identity exists in the case of other solutions. The simple relations which have been obtained in a relatively short time by a study of the electrolytic phenomena would have taken an immense amount of time if we had attempted to obtain them from a study of chemical corrosion alone. In fact it is doubtful whether any satisfactory result would have been obtained without the electrolytic corrosion. This method is obviously applicable to all other alloys and should lead to important results, especially in the case of the steels."

Cushman[1] seems to have been the first to have emphasized the part that two phases may play in promoting electrolytic corrosion. He suggested that unequal distribution of manganese sulphide in fence wire might be one of the reasons why modern fence wire corrodes rapidly. This point of view was developed more in detail[2] as time went on. "In considering the corrosion of iron it is important to remember that iron is a metal which readily combines with or dissolves nearly all the other elements. With possibly one or two exceptions, there are no elements that do not either dissolve in or combine readily with iron. It is also unique in the fact that very small quantities of impurities suffice to entirely change its physical characteristics. On account of this fact metallurgists scrutinize the hundredths of a percent of some of the principal impurities that are generally associated with this metal. This is particularly true, for instance, of the element phosphorus. It is so important to modern metallurgy that the amount of phosphorus should be controlled in certain forms of steel that an animated discussion is going on at the present

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[1] Department of Agriculture. Farmers' Bulletin No. 239 (1905).

[2] Cushman: Trans. Am. Electrochem. Soc. 12, 403 (1907).

time between certain interests as to the control of the amount of phosphorus that steel shall carry, and the question at issue amounts to no more than a few hundredths of one percent.

"Manganese is also an element which is nearly always associated in modern metallurgy with iron and steel. Manganese decreases the electrical conductivity of iron, and as the percentage of manganese, starting from zero, rises, the electrical resistance increases up to a certain specific maximum. You will see that if the presence of manganese in iron raises the electrical resistance, any change in the distribution of the manganese means that there will not be a constant electrical conductivity throughout its mass, or on any given surface. One who is familiar with the methods of modern metallurgy that the manganese is added for certain specific purposes, not as a rule quantitatively, but in accordance with the views of the iron master who has control of the mill or furnace. Moreover, the manganese is usually added by throwing lumps of ferro-manganese into the molten metal, either in the furnace itself, or in the ladle into which it has been poured. Chemists know the extreme care that has to be taken in order to get uniform mixtures of substances in the course of chemical operations. In the large scale of metallurgical processes, even if it were possible to take great care in the mixing, it still happens that when iron is cooled from the molten state, segregation takes place; that is to say, the impurities, although they may have been thoroughly mixed in the molten mass, do not remain homogeneously distributed after the metal is cooled.

"For these reasons we must remember that in studying iron and steel from the standpoint of their stability, under the conditions of service, we are not dealing with homogeneous pure metal. It is not difficult for an electrochemist to believe that when such material is immersed in, or even brought into contact with, an electrolyte, electrolysis will take place upon the surface, and thereby induce rapid corrosion. It is probable that the corrosion of all metals is more or less due to electrochemical action. Before metals can be attacked at ordinary temperatures in the presence of water they must first pass into solution, and in passing into solution become ionized. This is true of copper, zinc, lead and the other metals that suffer corrosion.

"In accordance with the conceptions of Nernst and the modern theory of solutions, all metals have a certain solution pressure which will operate until counterbalanced by the osmotic pressure. Iron, however, appears to differ from the other metals in one important respect. The corrosion of iron does not take place evenly and uniformly over the surface. On the contrary, it is a matter of common observation that iron corrodes rapidly at certain weak points, the effect produced being known as pitting. That this effect produced by local electrolysis would hardly be doubted, even if it were not possible to demonstrate it by the use of the ferroxyl indicator.

"Early in this investigation the writer observed that whenever a specimen of iron or steel is immersed in water or a dilute neutral solution of an electrolyte to which a few drops of phenolphthalein indicator has been added, a pink color is developed. If the solution is allowed to stand perfectly quiet, it will be noticed that the pink color is confined to certain spots or nodes on the surface. The pink color of the indicator is a proof of the presence of hydroxyl ions and thus indicates the negative poles.

"Since phenolphthalein shows only the nodes where solution of iron and subsequent oxidation can not take place, Dr. W. H. Walker suggested the addition of a trace of potassium ferricyanide to the reacting solution, in order to furnish an indicator for the ferrous ions whose appearance marks the positive poles. If iron goes into solution, ferrous ions must appear, which, with ferricyanide, form the well-known Turnbull's blue compound. Going a step farther, Walker suggested stiffening the reagent with gelatin or agar-agar, so as to prevent diffusion and preserve the effects produced. For this combined reagent, which indicates at one and the same time the appearance of hydroxyl and ferrous ions at opposite poles, the writer has suggested for the sake of brevity the name "ferroxyl." If the reagent has been properly prepared the color effects are strong and beautiful. In the course of a few days the maximum degree of beauty in the colors is obtained, after which a gradual deterioration sets in.

"In the pink zones, as would naturally be expected, the iron remains quite bright as long as the pink color persists. In the blue zones the iron passes into solution and continually oxidizes, with a resulting formation of rust. Even the purest iron develops the nodes in the ferroxyl indicator, but impure and badly segregated metal develops the colors with greater rapidity and with bolder outlines. This result would of course be expected, as in pure iron the formation of poles would be conditioned by a much more delicate equilibrium than in impure iron, where changes in concentration of the dissolved impurities would stimulate the electrolytic effects.

"In the writer's opinion these effects which are produced in the ferroxyl indicator constitute a visible demonstration of electrolytic action taking place on the surface of iron, and causing rapid corrosion at the positive nodes."

One difficulty with the ferroxyl indicator is that it is too sensitive. Walker[1] points out that "if a piece of chemically pure iron free from mechanical strains and without evident crystallization, be immersed in the ferroxyl indicator, the positive and negative zones will be apparent after a few moments. There appears to be an unequal concentration of oxygen or segregation of oxygen upon the surface, which cannot be explained by discernible differences in the character of the surface. If the ferroxyl indicator be removed, the surface cleaned by rubbing with a dry towel, and the indicator again applied, the same separation into zones is seen, though in an entirely different configuration. The indicator is apparently a very delicate one and susceptible to changes in equilibrium, which up to the present have not been detected by other means."

Walker goes on to say that "since corrosion is manifestly an electrochemical action, it seemed probable that if two specimens of iron were selected, one of which had proven itself in practice as especially resistant to corrosion, and another which had shown itself to be very susceptible to corrosion, certain

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[1] J. Am. Chem. Soc. 29, 1262 (1907).

differences in the electrochemical behavior should be discernible. Two sets of such specimens were obtained. The first consisted of two pieces of sheet metal which had been used as culverts in road building, one of which had given way in but a short time while the other was practically intact. The second set consisted of two strands of wire from a piece of ordinary barbed wire fencing, one of which was badly corroded upon an exposure of but six months while its neighbor was apparently in its original condition. Nothing is known of the history of the two wires; the good piece of sheet was known to be from an open hearth steel ingot containing but a trace of manganese, and in the heating and rolling of which extra precautions had been taken to prevent segregation. The poor piece was known to be from an ingot of ordinary Bessemer steel.

"If corrosion be an electrochemical phenomenon depending upon the formation of an anode portion and a cathode portion and the passage of a current between these two, the rate of this corrosion may be assumed to be proportional to the difference of potential between the two surfaces."

The results showed that "areas having marked differences in potential exist in far greater number upon the surface of a piece of iron prone to corrosion than upon iron which is resistant to corrosion." Walker was careful to add, however, that "it is as yet too early to decide that measurements of this kind indicate the tendency of iron to corrode; but we hope to obtain definite information on this point by investigating a large number of specimens of known resistance to corrosion."

Since differences of homogeneity will tend to cause local voltaic cells and will therefore tend to cause corrosion, the natural corollary is that, if other things are equal, the most homogeneous metal will corrode the least rapidly. This is absolutely sound; but then people assumed, perhaps unconsciously, that other things were equal and that therefore the most homogeneous metal would corrode the least rapidly. This unwarranted assumption has done a great deal to retard the effective study of corrosion, because attention has been concentrated unduly on the question of homogeneity to the comparative exclusion of more important factors; and many people have believed that the electrolytic corrosion theory was justifiable only in case homogeneity was the most important factor in preventing corrosion.

In 1917 E. A. Richardson and L. T. Richardson[1] report on experiments on the relative corrosion of cast iron, steel, and pure iron. They conclude that "the results of this test agree with other tests and add to the evidence already accumulated, that the resistance of an iron to corrosion does not necessarily depend upon its purity or homogeneity, as would be indicated by the electrolytic theory of corrosion. The theory, in its present accepted form, does not explain the great resistance offered by cast iron to corrosion. While it may be true that the initial rusting is largely electrolytic in character, other factors, such as adherence of the rust and the protection thereby given to the metal, come into operation and outweigh any electrolytic corrosion—a conclusion that has also been arrived at by other observers."

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[1] Trans. Am. Electrochem. Soc. 31, 195 (1917).

There is nothing about the electrolytic theory of corrosion which precludes the formation electrolytically of insoluble and protecting coatings. The authors have substituted for the theory of electrolytic corrosion the narrow views of some of its protagonists. As was pointed out by Speller[1] in the discussion of their paper, their results do not in any way "throw discredit upon the electrolytic theory. Copper-steel has been mentioned, and here the longer life seems to be due to the formation of an oxide which adheres very tenaciously to the surface of the iron. Copper-steel and ordinary steel in the atmosphere act very much the same for the first few weeks, after which the corrosion of the copper-carrying steel is retarded very materially, and in some cases actually seems to stop."

We cannot criticize the Messrs. Richardson very severely for the attitude they took, wrong though it is, because even Walker,[2] four years later, seems to consider the effect due to homogeneity as the most important feature of the electrolytic theory of corrosion.

"The mechanism of corrosion is now fairly well understood. Whitney in 1900 showed it to be an electrochemical phenomenon, obeying the laws of electrochemistry. It was the privilege of the writer to demonstrate in 1907 the function of oxygen in corrosion, and to apply the experimental facts to the preservation of many engineering structures. The engineering public, however, has been slow in availing itself of the published work on corrosion probably for a number of reasons. First, the entire literature of corrosion is full of apparent contradictions and obvious mis-statements. This is occasioned by the fact that corrosion is a most complex phenomenon and that factors which may be controlling in the results are frequently overlooked. No two men have the same sample of iron and steel; the heat treatment is generally different, the analysis imperfectly known; the state of the surface and the finish is neglected, and a host of other important conditions completely ignored. No wonder the results present discrepancies, and the public fails to show an interest in them. Second, certain conclusions which in the early days seemed to follow logically from the electrochemical theory of corrosion have been shown to be erroneous, and have led to disappointing results. Possibly the logic was false; but at any rate we cannot crown the theory with any far-reaching beneficial results. If I may paraphrase, "the evil that a theory does lives after it; the good is oft interred with its bones." The theory that the earth was flat delayed the discovery of America by a number of centuries; the phlogiston theory guided experimenters to fruitless fields of investigation and wasted much valuable time and energy. And so with the doctrine that homogeneity of structure in iron and steel, insures an absence of corrosion. The public is still told through advertising propaganda that the old Newburyport bridge withstood Atlantic Ocean storms for over one hundred years because the iron with which it was built was pure and homogeneous, when, as a matter of fact, the majority of the links of the great chains were very impure and extremely heterogeneous. The further fact that when these very pure links were

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[1] Trans. Am. Electrochem. Soc. 31, 199 (1917).
[2] Trans. Am. Electrochem. Soc. 39, 53 (1921).

rolled down to sheet form and exposed to the weather, they rusted like modern iron and disappeared in a few years, is conveniently ignored. The old blacksmith's forge apparently introduced an element of protection which has not yet been predicted by the electrochemical theory nor realized by laboratory experimentation.

"Corrosion may be divided into two classes—that taking place in the atmosphere with free access of the oxygen of the air, and that in positions from which the air is or can be excluded. In the first field the work of Mr. D. M. Buck stands pre-eminently the greatest contribution made in the art of preventing corrosion since the introduction of hot galvanizing. Impartial evidence is now legion that no commercial iron or steel so well withstands atmospheric corrosion as does steel containing approximately 0.2 percent copper. When thus alloyed even the much maligned Bessemer steel excels in resistance to corrosion the widely-heralded, pure, open-hearth iron. Unfortunately, copper-bearing steel is not a child of the electrolytic theory, although we have no doubt that when adequate explanation of the wonderful effect of this small amount of copper is finally suggested, it will be found to be essentially electrochemical. With the unbroken record of successful achievement now possessed by copper-bearing steel, and the low cost of metallic copper, there seems to be no excuse for the fabrication of those structures which must withstand exposure to the weather, from any other material.

"But a copper-bearing steel produces its own protective covering only when the oxygen concentration is high. When the amount of oxygen is limited, as when the structure is immersed in water, other protective means must be found. If all of the oxygen in a system could be removed, corrosion would cease. This fact was early recognized by Mr. F. N. Speller, and the careful experimentation carried on by him during the last twelve years in the application of this principle to the preservation of engineering structures, is now being crowned with success. Enough operating data from large installations are now available to demonstrate the effectiveness of this method of conserving iron and steel."

This statement by Walker called forth a rather bitter reply from Cushman.[1] "It is of course perfectly natural that Dr. Walker should have become a strong proponent of the copper alloy theory in corrosion resistance, and it is noteworthy that he now deserts the so-called electrolytic theory of corrosion and seems to point out that homogeneity of structure of iron and steel is not worth while, from a corrosion standpoint. My own recollection is, and I think the record will show, that Dr. Whitney neither formulated a theory nor attempted to prove anything. He published, as I recollect it, a short paper, in which he suggested, as the result of a passing observation, that the corrosion of iron might be explained or linked up to the Arrhenius, van't Hoff, and Nernst conceptions of the theory of solutions. Dr. Whitney stated that this suggestion might be sustained by careful research which he thought worth while. He did not, however, pre-empt the field, but put his suggestion out as an invitation to men who had more time to enter this field of investigation.

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[1] Trans. Am. Electrochem. Soc. 39, 57 (1921).

Dr. Walker has cited a number of authorities who sustain his views on copper-bearing steel, but he chooses to ignore by citation any workers in the field who disagree with his opinions. Dr. Walker states that in 1907 he had the privilege of demonstrating the function of oxygen in connection with corrosion. I may state that in 1905 and 1906 I had already demonstrated, by the use of phenolphthalein the formation of electropositive and negative nodes whenever iron or steel is rusting. This led to the development of the ferroxyl test which proves electrolytic action. Now a thing that is proved is not a theory. The electrolytic explanation of corrosion is not to be evaded or avoided, no matter whether it coincides with an individual bias or prejudice or not."

It is to be noticed that Cushman's statement that "the electrolytic explanation of corrosion is not to be evaded or avoided" is perfectly true but does not show that homogeneity is necessarily the important factor or even a desirable factor. In the discussion Walker[1] says that "it is obvious from a reading of my paper that not only have I not abandoned the electrolytic theory of corrosion, but that I predict that when the explanation for the remarkable behavior of small amounts of copper in reducing corrosion is explained it will be found to be essentially electrochemical. Certain conclusions which at first seemed to follow from the electrolytic theory of corrosion have now proven themselves erroneous."

It is rather curious that the delusion as to homogeneity being the most important point should have taken hold of people so firmly, because Walker[2] pointed out years ago that a continuous coating would protect iron even though the coating were a material which would accelerate corrosion when placed in contact with the iron. "I have already shown that mill scale, or magnetic oxide of iron, is strongly electronegative to iron. Since mill scale is insoluble in water and cannot of itself enter into the reaction, its only function can be analogous to that of platinum or other insoluble conductor of this kind, viz, to furnish a surface on which the hydrogen liberated by the dissolving iron can separate and be catalytically oxidized to water again. This is also true of the black oxide protective coatings sometimes used upon iron and steel, as, for example, that of the Bower-Barf process. Just as is the case in mill scale, these coatings are very serviceable so long as the whole coating is intact. But so soon as a portion of the metallic iron is exposed, this portion corrodes all the more rapidly on account of the presence of the surface of scale on which the oxidation of the hydrogen and consequent depolarization can go on. The inevitable result is that a 'pit' forms at the exposed point and grows deeper and more marked in proportion as the scale is dense and closely adherent to the iron surface. Hence, if it were possible to remove the mill scale entirely from steam boiler tubes, for example, pitting would be largely eliminated, and the life of the tube prolonged."

Attention seems to have been focussed on the disadvantage of a break in the protecting coating of this type and people have rather overlooked the

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[1] Trans. Am. Electrochem. Soc. 39, 59 (1921).

[2] Trans. Am. Electrochem. Soc. 14, 181 (1908).

possibility of a self-healing coating such as we actually have on aluminum and on nickel. The new stainless steel owes its properties to a coating of this type.

Lambert,[1] in England, has made out an astonishingly good case for the non-corrodibility of a homogeneous metal. "The impurities contained in the best commercial iron must, from a chemical point of view, be regarded as considerable, and, in the light of our present knowledge of the great modifications capable of being produced in the properties of substances by the presence of even minute traces of impurities, it cannot be contended that experiments with impure iron afford trustworthy grounds for a satisfactory theory of the oxidation of iron.

"The aim of the present investigation, was to bring together, under the simplest possible conditions, the purest obtainable water, oxygen, and iron, in vessels which would be least likely to be acted on by any of these substances. . . .

"The choice of the kind of vessel in which to carry out the experiments was the cause of much difficulty. It was finally decided to use vessels made of transparent fused silica as being least likely to be affected by either water, iron, or oxygen. After many trials and experiments, a simple form of glass vessel was devised, which, with a tube of clear fused silica, gave all the advantages of an apparatus made entirely of silica, since the water which collected in the silica tube and came in contact with the iron must have condensed on the inside of the silica tube itself. . . .

"The material employed in the preparation of pure iron was a pure specimen of 'Kahlbaum' ferric chloride. The salt was found to be free from sulphate, arsenic, alkali, or alkaline earth metals. A solution of the salt was made in conductivity water and electrolysed between electrodes of pure iridium foil. This method is made possible by the fact that pure iridium is not attacked by chlorine, which is evolved at the anode. The metallic iron which was deposited on the cathode was then thoroughly washed with conductivity water, and dissolved in pure dilute nitric acid. This solution of ferric nitrate in excess of nitric acid was concentrated on the water-bath, and the salt crystallized from the solution in concentrated nitric acid. The crystals were separated from the mother liquor, washed with pure concentrated nitric acid, and recrystallized four or five times from this solvent. The crystals so obtained were colourless, or white when seen in bulk. It is to be noticed that ferric nitrate, prepared from ordinary pure iron, has, when seen in bulk, a pale violet colour like that of iron alum, and that the colour cannot be removed by repeated crystallisation from pure nitric acid.

"The ferric nitrate crystals were transferred by means of a spatula of iridium foil to a pure iridium boat. The boat was then heated in air on a thick tile, so that the flame gases did not come in contact with it. The ferric nitrate was thus converted into the oxide or basic nitrate. The boat containing the flakes of oxide was then placed into a transparent silica tube, and heated in an electric resistance furnace to a bright red heat (just above 1000°), while

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[1] J. Chem. Soc. 97, 2426 (1910); 101, 2056 (1912); 107, 210, 218 (1915); Trans Faraday Soc. 9, 108 (1913).

a stream of pure hydrogen was passed through the tube.[1] . . . The hydrogen was prepared by the electrolysis of a solution of pure barium hydroxide. . . . The electrolytic cell contains two pairs of large platinum electrodes and is capable of producing a steady stream of hydrogen. The gas was passed through a U-tube containing lumps of pure sodium hydroxide, in order to remove excess of water vapour, and then through another U-tube containing tightly-packed glass wool.

"The metallic iron so obtained, by direct reduction of the flakes of oxide or basic nitrate, had a distinct metallic lustre and a light grey colour. If the flakes of oxide were ground in an agate mortar before being reduced, the iron produced by reduction was light grey in colour, but had little or no lustre. The properties of the two kinds of iron were the same."

"It was found that pure iron, prepared exactly as described above, did not undergo any visible oxidation when treated with pure water and pure oxygen in vessels made of clear fused silica, and that there was no change even after several months.

"If, however, ferric nitrate, prepared from ordinary pure iron, was used, even after ten recrystallisations, and iron made from it by precisely the same method, the iron invariably showed signs of oxidation in two or three hours, and, after twelve hours, there was always a considerable deposit of reddish-yellow ferric oxide on parts of the metal. Oxidation also took place even when the oxide prepared from the nitrate was strongly heated in a stream of pure oxygen for several hours before being reduced to the metal.

"It is impossible that iron prepared in this way can contain anything more than a very slight trace of impurity, and that impurity, whatever it may be, cannot be of such a nature that it is acid, or will give an acid on oxidation.

"Again, if platinum vessels were used, particularly if a platinum boat was used in which to reduce the iron, the iron produced readily underwent oxidation in two or three hours, and oxidation invariably took place at those parts of the metal which had been heated in contact with the platinum boat.

"Richards,[2] in his work on the atomic weight of iron, prepared iron in somewhat the same way as we have done, but he distilled the nitric acid used from a platinum retort, and employed platinum vessels throughout for his preparation. He states that the iron always contained slight traces of platinum, and that, when it was dissolved in acids, a small black speck of platinum remained.

"This small trace of platinum, which may be merely attached to the iron, or may be present in the form of a solid solution, would seem to be enough to cause oxidation to take place.

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[1] In some experiments the oxide was heated in a stream of pure oxygen for several hours before being reduced, in order to remove the occluded nitrogen which is contained in most oxides formed from nitrates. This operation, however, was found to be unnecessary, since the properties of the resulting iron were exactly the same as when the oxide or basic nitrate was directly reduced in hydrogen. The slight oxidation undergone by the iridium did not seem to affect the iron. The occluded nitrogen was undoubtedly removed by heating in hydrogen to the high temperature of the furnace. This temperature was between the melting point of silver and that of copper.

[2] Proc. Am. Acad., 35, 253 (1900).

"All kinds of commercial iron which were used readily rusted under the same conditions of experiment, as also did iron made with the most scrupulous care by many other methods.

"A specimen of commercial electrolytic sheet iron (99.9 percent of iron), which had been polished and treated with a 1 percent solution of chromic acid for three months, and afterwards washed with pure water and quickly dried, readily rusted under the same conditions of experiment. This method of treating ordinary iron is said by Moody to remove the impurities from the surface of the iron. It seems probable that other reasons must be sought for the non-rusting of the commercial iron used by Moody under his precise conditions of experiment.

"It would seem to be proved from these experiments that pure iron will not undergo visible oxidation in contact with pure water and pure oxygen, but that a small trace of impurity in the iron is sufficient to cause oxidation under exactly the same conditions of experiment, even if this impurity be not of an acid nature or likely to produce an acid during the reaction."

In the second article Lambert[1] says that "pure iron has been kept in contact with pure water and pure oxygen, under atmospheric pressure, for more than two years without showing any signs of corrosion or alteration of any kind. Further, ordinary air can be substituted for pure oxygen and ordinary tap-water for pure water, and the result is the same—the surface of the metal remains bright and untarnished for an apparently indefinite time. The explanation of this fact is to be sought in the greater homogeneity of the iron, due to its purity. If such iron be really homogeneous, and all parts of it have the same solution-pressure, then, on the above theory, a piece of metal placed in contact with an electrolyte will not furnish the conditions for the production of an electric current; since there is nothing to bring about the passage of an electric current, the iron cannot therefore pass into solution and no corrosion can take place. It does not necessarily follow from the fact that the iron does not rust that there must be perfect homogeneity in the metal. It may be that differences of electric potential do exist on the surface of the iron, but they are so much smaller in this iron than in any commercial varieties of the metal that, in the presence of water and oxygen the electric current which passes between the points of different solution-pressure is so small that the amount of iron passing into solution is not sufficient for the formation of a perceptible amount of rust even after long periods.

"A striking confirmation of the truth of this argument is afforded by the following experiment: Some pieces of pure iron which had been exposed to water and air for several months without showing any signs of corrosion were carefully dried between Swedish filter papers. Some of the pieces were then placed in a polished agate mortar and pressed strongly with an agate pestle, whilst others were left untouched. All of them were then again put in contact with water in silica tubes and exposed to air. The pieces which had been subjected to pressure in the agate mortar showed signs of corrosion in less than an hour, and after several hours a golden-yellow deposit of rust had formed

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[1] J. Chem. Soc. **101**, 2068 (1912).

on those parts of the iron which had not been pressed, whilst the parts which had been pressed by actual contact with the agate remained quite bright. Those pieces of iron which had not been pressed showed no signs of corrosion, proving that the process of drying had not been the cause of the striking alteration in property of the pieces which had been put under a strain.

"The pieces of metal which had been subjected to pressure consisted of two modifications of iron, a pressed part and an unpressed part. These two varieties of iron would have a different solution-pressure, and so, when placed in contact with the electrolyte water, would constitute a self-contained galvanic element. The fact that rust formed on the unpressed part showed that iron passed into solution at that part, which was therefore relatively electropositive to the pressed part.

"That the pure iron is not absolutely homogeneous—that it does possess electrically different parts—is indicated by its behaviour toward acids and towards solutions of salts of the alkali metals in the presence of air or oxygen. These reactions are still under investigation, and can only be considered very briefly at present.

"It may be said generally that cold dilute sulphuric and nitric acids have very little visible action on the metal, but that even very dilute cold hydrochloric acid causes the slow evolution of bubbles of hydrogen. The metal readily dissolves in all three acids on warming, but, again, hydrochloric acid is much more vigorous in its action than the others.

"The action of solutions of alkali salts on the metal in contact with air shows many irregularities which still await investigation. Pure iron which had been exposed to the action of water and air for many months without showing any signs of rusting, underwent corrosion in a few hours when transferred to a normal solution of sodium chloride in air.

"That other constituents of the air besides oxygen play no part in this reaction is shown by the fact that corrosion took place just as readily when pure oxygen was used.

"The chlorides of potassium and ammonium seem to have a similar action, but, curiously, the corresponding sulphates and nitrates behave differently. The pure iron may be exposed to concentrated solutions of the sulphates and nitrates of sodium, potassium and ammonium in the presence of air, often for many days, without undergoing much corrosion.

"It seems quite possible that the study of the action of salt solutions on pure iron may bring to light some definite evidence for the view held by the author that a considerable factor in determining the corrosion iron is the alteration in the electrical character of the different parts of the metal brought about by the action of salts and acids.

"It is well known that all ordinary forms of iron, when placed in contact with solutions of copper salts, are immediately covered with a deposit of metallic copper. It is only when the metal has been rendered 'passive', by one of the many processes which produce this condition, that iron can be made to remain unaffected in a solution of a copper salt. The copper salt solution must be very dilute, and even then the passive iron recovers its ordinary behaviour after several hours, and causes copper to be deposited on it.

"Pure iron will withstand the action of a saturated solution of copper sulphate or copper nitrate, at the ordinary temperature, for an apparently indefinite time, without losing any of its metallic lustre and without any perceptible trace of copper being deposited.

"Some specimens of iron which had been exposed for several months to a concentrated solution of copper sulphate were removed, washed, and dried, and examined under the microscope. The curious structure of the surface was exactly the same as it was before the iron was placed in contact with the copper sulphate solution.

"Pure copper sulphate, free from iron, was used, and the solution after being in contact with the iron for many months failed to give any test for the presence of iron.

"If the temperature of the copper sulphate solution is raised to that of boiling water, deposition of copper on the iron slowly occurs, and finally, after some hours, the iron passes into solution completely, and copper is left behind in the form of very small crystals.

"Copper is also deposited on the iron if it is pressed in an agate mortar before being put in the solution of copper sulphate, or if it is pressed with a quartz rod while under the copper sulphate solution.

"The behaviour of the pure iron towards copper chloride is, however, quite different. If a concentrated solution of copper chloride is used, the iron becomes coated with copper immediately it is put into the solution, and, within a few minutes, the iron all disappears, and only finely divided copper remains.

"If a very dilute solution (less than one percent) of copper chloride is used, the action is slower. For a few seconds the iron retains its brightness; then dull spots are seen at some points on the surface of the metal; these quickly spread over the whole surface of the iron, and the reaction proceeds to an end, as before, in a remarkably short space of time.

"The experiment is perhaps even more striking if carried out in a vacuum. The finely divided copper, which is left after the first reaction, slowly dissolves, and finally white, insoluble cuprous chloride is left.

"Similar results are obtained if a solution of sodium chloride is added to solutions of the sulphate and nitrate of copper.

"Ordinary metallic aluminum behaves in much the same way towards solutions of copper salts. The metal is not affected by solutions of copper sulphate or copper nitrate, but, if copper chloride is used, or if sodium chloride is added to the solutions of copper sulphate or nitrate, precipitation of copper on the aluminum immediately follows.

"This behaviour of aluminum has been attributed to the fact that the metal, under many conditions, becomes coated with a protective film of hydroxide or basic salt.

"It is assumed that this protective film is more readily soluble in the hydrochloric acid produced by the hydrolysis of the copper chloride than in the sulphuric or nitric acids from the sulphate or nitrate respectively. This argument is strengthened by the fact that aluminum is readily dissolved by hydrochloric acid, whilst it is practically unaffected by sulphuric or nitric acids even at 100°.

"Experiments have shown that the same arguments cannot possibly hold good in the case of pure iron.

"It is very improbable that iron prepared by the reduction of the oxide by hydrogen at a high temperature, and allowed to cool in the gas, would have a film of oxide on the surface, and, on account of the irregularity in the shape of the pieces of iron, it is unlikely that such an oxide film, if it existed, would form a complete, unbroken protective coating.

"Nevertheless, the presence of some kind of protective coating on the iron, capable of being dissolved by cold dilute hydrochloric acid or nitric acid under the same conditions, would explain why copper is deposited from a solution of copper chloride and not from copper sulphate or copper nitrate solutions; it would explain, too, why iron when subjected to pressure under copper sulphate and copper nitrate solutions causes the deposition of copper on it, for pressure might bring about a disruption of such a film; and further, it might be considered as an explanation of the fact that rise of temperature will cause copper to be deposited on the iron from copper sulphate and nitrate solutions, on the ground that such a film would be more soluble in hot than in cold acids.

"There are two possible kinds of protective films which might conceivably be present on the surface of the pure iron, namely, (a) an oxide film produced by the reversible decomposition of small traces of water in the hydrogen used for the reduction of the iron oxide to iron, and (b) a protective layer of some hydride of iron produced by the absorption of the hydrogen as the metal cooled down in the gas.

"Careful experiments have been made to test these possibilities. The hydrogen used for the reduction of the iron oxide was dried by passing it through a long tube containing phosphoric oxide, so as to remove all but the most minute traces of water, and then the iron which was produced was brought in contact with copper sulphate solution whilst it was still in the atmosphere of hydrogen. The copper sulphate solution itself had been previously saturated with pure hydrogen. There was no deposition of copper on the iron, which remained quite untarnished in the solution.

"Other specimens of iron were prepared and allowed to come in contact with the air before they were cold. A thin, yellow layer of oxide was formed on the metal, but this slightly oxidised metal caused the immediate deposition of copper when placed in contact with a solution of copper sulphate.

"It is probable that, as suggested above, the oxide film does not form a complete protective coating; in such a case there would be differences of potential on the surface of the iron, and we should expect copper to be deposited.

"It must be concluded, then, that the non-deposition of copper by the pure iron from copper sulphate and copper nitrate solutions cannot be accounted for by the presence of a protective oxide film on the metal.

"That the same argument holds good in the case of a possible protective film of hydride is proved by the fact that specimens of the metal which had been heated in a clear silica tube for several hours, at about 1000° in a vacuum, until spectroscopic tests showed that all the hydrogen had been removed, behaved in all respects as before—they remained quite bright and unaffected in contact with saturated solutions of copper nitrate and copper sulphate, but caused the immediate deposition of copper when placed in very dilute solutions of copper chloride.

"The behaviour of the iron under different conditions towards solutions of the sulphate and nitrate of copper can be readily explained on the basis of an electrolytic theory, but the extraordinary behaviour of the metal in copper chloride solutions is mysterious.

"We have seen that the chlorides of the alkali metals have a very remarkable action in starting and promoting the rusting of the pure iron in air, and it may be that soluble chlorides have the power, in some way or other, of increasing the electrical differences which exist in the iron. If the chloridion has such a property it would also explain this curious behaviour of copper chloride. For the present this must be left an open question.

Cushman[1] has stated that no iron has been found of such purity that it gives no trace of positive and negative nodes in the ferroxyl indicator; but Lambert's "pure iron remains quite bright, and causes no formation of positive and negative nodes when left in contact with the reagent for an indefinite time. If a piece of the pure metal is subjected to pressure, however, it behaves like other kinds of iron when put in contact with ferroxyl reagent. A pink colour develops in the jelly around the pressed part, and Turnbull's blue is formed round the parts which have not been subjected to pressure."

While this is a very good piece of work, the author has proved too much. On any point of view copper will precipitate on iron unless the iron is covered with a film of some sort. All the experiments indicate the existence of a film. On the other hand the experiments to determine the nature of the film gave negative results. Consequently they are either faulty in some way or they do not cover the ground. It would have been interesting if Lambert had determined the electromotive force of his pure iron. This is not essential however and the film which keeps the copper sulphate solution from acting is quite sufficient to keep the metal from corroding. It seems practically certain that the film is an oxide film formed in the reduction experiments when the copper sulphate solution came in contact with the iron. It must be admitted, however, that it is not clear why rusting should take place at the unbruised portion rather than at the bruised portion.

The experiments with lead[2] are also very interesting even though one cannot accept the author's conclusions. "Many methods were employed to prepare lead in a high state of purity previous to its distillation in the manner described above; but it was found very difficult to remove all traces of iron.

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[1] "Corrosion and Preservation of Iron and Steel," 49 (1910).

[2] Lambert: J. Chem. Soc. 107, 210 (1915).

Finally, lead was prepared by the method described by Stas.[1] It was cut into small chips by means of a pure iridium spatula on to which a cutting edge had been ground.[2] The lead was then distilled in clear quartz tubes, which were about 7-8 mm bore and 25 cm long, and were divided into three compartments by narrowing the tube down to capillaries. The tubes were exhausted while the metal was kept in the molten state, and finally the lead was distilled at about 1200°. The first fraction was collected in the first compartment which was then sealed off. The middle fraction was collected in the second compartment, whilst the residue was left behind in the third compartment. It is worthy of note that the globules of lead obtained in this way adhered very closely on the under side to the quartz, producing a very fine reflecting surface. It was found that if the distilled lead was exposed to air a short time after distillation, but when quite cold, the brilliant surface was quickly dimmed by a film of oxide. If, however, the metal was kept in the vacuous tube for several months, exposure to the air did not then cause any appreciable decrease in its brilliant lustre for several days. It was only the middle fraction of lead that was used in the experiments described above."

In another experiment water was distilled into the vessel within twenty-four hours after the distillation of the lead and then the vessel, containing only pure lead and pure water in a vacuum, was sealed off and set aside for twelve months. "After the lead in the first vessel had remained in contact with water in a vacuum for twelve months the metallic lustre of the metal was quite unaffected. The point of one of the capillaries was then broken off in an atmosphere of pure oxygen, and the gas thus allowed to come into contact with the lead and water. For more than a week there was no visible tarnishing of the brilliant metallic surface of the large globule of lead which was under the surface of the water, but after that time the metallic lustre was gradually dimmed by the formation of a dark-coloured coating of oxide on its surface. The rate of corrosion was, however, so slow that after more than six months' exposure to the combined action of water and oxygen the layer of oxide was thin enough to display interference colours. After exposure for nearly a year the globule of lead is covered with a layer of a dark brown oxide, and minute crystals of hydrated lead oxide can be seen in the water."

Lambert considers that lead probably exists in different modifications, the more instable forms predominating in the freshly distilled metal and giving it a heterogeneous character, which will tend to disappear with time owing to the conversion of the instable forms into the stable one.[3] "When the metal is kept for a long time in a vacuum, it will become more homogeneous as far as its physical character is concerned, and consequently the rate at which it will pass into solution in water in the presence of oxygen will be greatly decreased."

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[1] Bull. Acad. roy. Belg. 10, 295 (1860).

[2] Pure iridium is so hard that it is possible to grind a sharp cutting-edge on to a plate of the metal.

[3] Since room temperature is an annealing temperature for lead, the instable form may have been lead under strain.

Lambert[1] draws the following conclusions from his work:—

"(1) Pure lead which has been distilled in a vacuum undergoes very rapid corrosion when subjected to the action of pure water and pure oxygen within a short time of the distillation of the metal. Chemical tests fail to show the presence of lead in solution before the addition of oxygen.

"(2) If the lead prepared in this way is kept for long periods in water, in a vacuum, before the oxygen is added, the rate of corrosion is enormously decreased.

"(3) Pure lead which has been distilled in a vacuum, and kept for some months, can be exposed to ordinary air for many days without any appreciable diminution of its brilliant metallic lustre, but more prolonged exposure causes the gradual formation of a dark-coloured oxide on the surface of the metal. The pure, distilled lead resembles silver or mercury in appearance, and shows none of the blue or bluish-grey colour usually associated with metallic lead.

"(4) The electrolytic theory of corrosion is applicable to lead. The passing of the metal into solution, which precedes corrosion, is due to electrolytic action between the electrically different parts of the mass of lead. In the case of chemically pure lead, the physical heterogeneity (due to the presence of different allotropic modifications of lead in the mass of metal) causes parts of the mass to be electrically different from other parts, and these electrical differences persist for a long time after the preparation of the metal."

In this work Lambert has violated the first canon of research. It is legitimate to postulate allotropic modifications of lead. In view of the experiments of Baker[2] on the behavior of dry mercury and dry benzene, it is perhaps legitimate to assign any properties one pleases to pure lead. These are assumptions *ad hoc*, however, and must be justified independently. The author has not done this. He is also in error in saying that his results "afford very strong evidence of the electrolytic theory of corrosion." There is nothing in this theory, when applied properly, which requires that a homogeneous metal should be inert in the presence of a depolarizer like oxygen. The potential difference between silver and silver nitrate may be, and doubtless is, modified by the presence of impurities in the silver; but nobody would claim that we did not have reversible equilibrium between a silver nitrate solution and an absolutely pure and homogeneous sheet of silver. It is much more reasonable to assume that, on long standing in an alleged vacuum, a film forms on the lead which is more resistant than the oxide film which forms more rapidly. Lambert has overlooked another point. In presence of water and oxygen his lead oxidizes slowly while his iron does not. For this to be true the iron must be more noble than the lead or it must be covered with a more resistant film. Very pure iron may be a metal as noble as silver; but this seems distinctly improbable and certainly requires proof. If pure iron has as low a solution pressure as silver, impurities must increase the solution pressure enormously which is very interesting if true. We must reject Lambert's conclusions on the grounds that he has given no independent confirmation of his

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[1] J. Chem. Soc. 107, 217 (1915).

[2] J. Chem. Soc. 121, 568 (1922).

postulates, that his conclusions are mutually inconsistent, and that his results are not in accordance with the electrolytic theory of corrosion though he says they are. With these obvious errors of omission and commission the probability of his also going astray in some less obvious manner becomes painfully great. In any event his results are purely of academic interest so far as the problem of corrosion is concerned, because he finds that iron and lead of very high, though not the highest, purity behave as they should and corrode in the presence of water and oxygen.

The function of oxygen as a depolarizer was pointed out by Walker[1] sixteen years ago. "One fact regarding the corrosion of iron appears to be undisputed, viz., that oxygen is necessary for a continued action. This corrosive action can cease from two causes, viz., the osmotic pressure of the dissolved iron may increase until it neutralizes or compensates the solution pressure of the metallic iron; or the action may be stopped by the separation of a film of molecular or gaseous hydrogen[2] upon the metal, which, owing to its resistance, prevents the flow of an appreciable current. From the fact that iron possesses, even in relatively concentrated solutions of iron salts, a very appreciable potential, it would seem highly improbable that the solution of the iron in water should be stopped by the osmotic pressure of that already dissolved, and therefore, although the oxidation and subsequent precipitation of the already dissolved iron is the most striking function of the oxygen, it is probably by far the least important, and its real accelerating action lies in the destruction of the hydrogen film already separated out on the surface of the metallic iron."

In a later paper Walker[3] says that the "accelerating action of metals such as platinum, copper, and lead, and materials such as coke and millscale upon the corrosion of iron is undoubtedly due alone to the aid these bodies offer to the elimination of the hydrogen produced by the corrosion reaction, owing both to the low over-voltage of hydrogen upon these substances and to the high catalytic action of these materials on the hydrogen-oxygen reaction by which the deposited hydrogen film is removed.

"While in specific cases the corrosion of iron can be absolutely controlled by first one and then another of these factors influencing it, too little attention is generally paid to the last one. The retarding action of the hydrogen film which is stable in the absence of oxygen and any acid-forming compound is so controlling that, from this point of view, oxygen (or air) may be said to be the cause of the corrosion. If oxygen be removed completely from boiler feed-water, the boilers will not pit or corrode. If oxygen be separated from the feed of ordinary hot-water supply lines, the 'red-water plague' and other corrosion troubles will disappear.

"By this removal of the cause of the disease, not only are all its ill effects avoided; but the necessity of drugging with alkali, removal of the products of corrosion and such curative measures, with their attendant evils, are elim-

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[1] Trans. Am. Electrochem. Soc. **14**, 179 (1908).

[[2] Walker has overlooked the polarization effect due to over-voltage (monatomic hydrogen).]

[3] Trans. Am. Electrochem. Soc. **29**, 436 (1916).

inated, and in this, as in so many other cases, experience has proved prevention to be better than a cure. If electrical and mechanical engineers will only take more closely into their confidence their brother electro-chemists, we can together more quickly make available the knowledge on the subject of corrosion already at our command for the elimination of the difficulties which corrosion introduces into commercial practice."

In line with this Speller[1] says that "the electrolytic theory of corrosion as formulated in 1903 by Dr. Whitney has led to the development of certain protective systems which are based on the removal of dissolved oxygen from water. Careful experiments in the Research Laboratories of the Massachusetts Institute of Technology and the National Tube Company have demonstrated that the amount of corrosion found is almost directly proportional to the amount of oxygen in solution and varies directly as the temperature. The predominating influence of free oxygen in water was suspected before this as a result of the early study of pipe corrosion, for the most striking fact in practical pipe experience is that hot-water *heating* systems invariably show no corrosion to speak of after thirty-five or forty years use whereas frequently hot-water *supply* systems operating at the same average temperature with the same water last only six or eight years. That this was independent of whether the material was iron or steel was fully demonstrated by many service tests which were conducted for a period of over ten years, in which representative pipes of each class were installed alternately in hot water lines." Quite remarkable results have been obtained when all the oxygen is removed from a hot water system either by a vacuum process or by chemical combination.[2] "If the water space of the heater is filled with thin steel lathing or if the water be made to flow through another tank containing steel scrap in this form, the residual oxygen will be fixed in a few minutes. Water so treated is practically inactive towards iron, and may be used in boilers or steel economizers without fear of corrosion so far as the water is concerned. Other metals may be used for oxygen removal, such as zinc; but iron is the most economical, not only because of its low first cost but for the reason that the ferrous hydrate formed removes an equivalent of oxygen in addition to oxygen taken up by the hydrogen."

W. D. Richardson states that "oxygen is of the utmost importance in promoting the continuance of corrosion by acting as a depolarizing agent, and this action is particularly prominent in the corrosion of iron and its alloys. If, however, the hydrogen active in corrosion is liberated at corrosion cathodes with low over-voltage, polarization supervenes less readily and corrosion proceeds at a greater velocity than in the case of a comparatively pure metal containing no suitable corrosion cathodes in its composition. Oxygen is more necessary to, and causes greater acceleration of, corrosion in pure iron than in an impure alloy such as cast iron, for in the absence of much oxygen relatively pure iron corrodes at an extremely low rate, but at a comparatively rapid rate

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[1] Trans. Am. Electrochem. Soc. 39, 141 (1921); J. Franklin Inst. 193, 515 (1922).

[2] Though not specifically so stated, dissolved carbon dioxide must also be removed. Trans. Am. Electrochem. Soc. 39, 64 (1921).

in the presence of oxygen. The opposite behavior of relatively pure iron when compared with cast iron under different conditions of corrosion is one of the most striking phenomena connected with the subject, and will probably afford illuminating data when correctly interpreted."

Messrs. Bengough and Stuart[1] dispute the depolarizing action of oxygen. "It is a well-tested experimental fact that no evolution of hydrogen gas from distilled water can be detected in the case of any of the metals mentioned above at the ordinary temperature, with the possible exception of magnesium. Even when the most careful microscopic search is made, none can be observed in the case of copper and zinc, as has been already reported[2] and recent work shows similar results for nickel and lead. With aluminum the evolution of hydrogen can be detected to a very limited extent in London tap-water, and quite readily if the metal be treated with mercury and then immersed in distilled water; in the latter case, the hydrogen evolved is chemically equivalent to the aluminum corroded. In this case, therefore, Reaction I appears to take place; but with these exceptions no direct evidence of the evolution of hydrogen gas has ever been found by the present authors, or been recorded in the literature on the subject, in the case of corrosion of ordinary massive metals from aluminum downwards in the electro-chemical list, in distilled water, conductivity water, or the specially purified water used by Lambert in his experiments on iron and lead. Nevertheless, under certain circumstances, all these metals may be very considerably corroded by the action of distilled water in the presence of atmospheric oxygen. There are two possible explanations for the non-appearance of hydrogen. The first and more usually accepted explanation is that the hydrogen is displaced by the metal electrolytically, but immediately oxidized by the oxygen of the atmosphere with formation of water. The conception is that of electrolytic cells dispersed over the surface of the metal, from the anodes of which metallic ions pass into solution displacing hydrogen, which appears at the cathodes, and is immediately oxidized by the atmospheric oxygen. A second possible explanation is that either no hydrogen is displaced, or that though displaced from solution it never reaches the gaseous form.

"To the first view, grave objections may be urged. In the first place, when hydrogen is actively evolved, as in the cases of magnesium and aluminum already quoted, it comes off from the seat of corrosion, such as a pit, and not elsewhere at a more or less distant cathode, as demanded by this theory. In the second place, A. M. Williams[3] has measured the depolarizing power of mixtures of oxygen and nitrogen at the ordinary temperature in the case of a silver-zinc cell, the mixture being allowed to play up the surface of the cathode of the cell. As compared with air, a 99 percent oxygen mixture gave an increased depolarization of 0.27 volt, and 55 percent oxygen of 0.165 volt; it is clear, therefore, that if air is a depolarizer, it is a very imperfect one. In the

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[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 72 (1922).

[2] Kahlenberg: J. Am. Chem. Soc., 25 (1903).

[3] J. Soc. Chem. Ind. 39 (1920).

third place, hydrogen can be collected quantitatively when displaced from acid by zinc in the presence of air, by magnesium from salt solutions, and by aluminum amalgam from distilled water, and this shows that little or none of the gas has been directly oxidized by the oxygen of the atmosphere to form water. The depolarizing action of atmospheric oxygen must be so slow in such cases, as compared with the rate of hydrogen production, that it is practically zero. In the fourth place, it has been found, in the case of zinc, that when the metal is placed in very dilute acetic acid (1 acid: 5000 water), the rate of corrosion by which it is comparable to that by distilled water, bubbles of hydrogen can be detected coming off from the surface of the metal; hence it is clear that at least part, and probably the whole, of the displaced hydrogen gas is not directly oxidized in the presence of water. But if the same sample of zinc be subsequently placed in distilled water, no evolution of hydrogen can be detected, yet the amount of zinc oxidized is approximately the same in the two cases if calculated over the whole area of the specimens, and much greater at certain localities in the case of distilled water than at any area in the acetic acid; hence the hydrogen should be more easily detected, if it be really evolved at such areas, in the distilled water than in the acid.

"Many cases could be quoted to illustrate the slowness with which cathodic polarization is removed in the absence of any depolarizer other than air, such for instance, as the necessity for the presence of potassium bichromate or nitric acid in the bichromate and Grove types of primary cell respectively, even though the cathode be of carbon, which should assist the oxidation of the hydrogen by adsorbed oxygen.

"If oxygen functions solely as a depolarizer, rapid circulation of the liquid over the metal should assist corrosion by increasing the rate of removal of the hydrogen film. Actually, Newton Friend has shown that an increase of water speed over the surface of the metal increases the rate of corrosion of iron only up to a limiting speed. If the speed be increased beyond this limit, the rate of corrosion rapidly falls. The latter result seems quite incompatible with the idea that the function of oxygen in corrosion is solely that of a depolarizer."

Mr. Speller informs me that hydrogen is found in their deoxygenated hot water systems and that iron will react with water, though slowly, to give hydrogen at lower temperatures. If zinc reacts with water in the absence of air, one of the products must be hydrogen. If air is present, there is no necessary reason why hydrogen should be given off. The criticism as to the evolution of hydrogen from aluminum and magnesium is not well taken because the anode and cathode reactions will always occur as close together as possible so as to make the resistance in the circuit as small as possible, so that speaking about "a more or less distant cathode" is either absurd or deliberately misleading. Nobody denies that oxygen under most conditions is a slow and unsatisfactory depolarizer. Even under the most favorable circumstances we can only draw very small currents from a hydrogen-oxygen gas cell because of the rapid polarization. In the experiments with zinc and dilute acetic acid, it is probable that the evolution of hydrogen prevents the oxygen from coming in contact with the metal after the initial depolarization. With zinc and water, the rate of corrosion is a function of the rate of diffusion of the oxygen among other things. The solubility and other properties of the corrosion products are also possible important factors. One cannot prove anything with experiments like this.

The paragraph in regard to the use of bichromate or nitric acid in primary batteries is quite pathetic. People draw from these batteries currents which are enormously greater than any which would correspond to the corrosion of ordinary metals under ordinary conditions. One ampere means over a gram of zinc per hour which would be an unheard of rate of corrosion.

There is some question as to the accuracy of Friend's work on the effect of stirring on the rate of corrosion of iron,[1] so that a discussion of it is unnecessary at the present time.

There is plenty of positive evidence as to the depolarizing action of oxygen, some of it coming from the opponents of the electrolytic theory of corrosion. Moritz Traube[2] has shown that the first reduction product of oxygen at the cathode is hydrogen peroxide and this has been confirmed by Richarz and Lonnes,[3] though one must not have too much oxygen[4] if one is to isolate the product. This is not disputed by Messrs. Bengough and Stuart[5] because they say specifically that it is very doubtful whether depolarization by atmospheric action takes place at all at atmospheric temperatures, except in special circumstances, such as the presence of platinized platinum. They are willing to concede some depolarization in presence of platinized platinum; but they deny its occurrence with any other metals. Unfortunately for this rather ingenuous view, Schönbein[6] showed that when lead amalgam is shaken with dilute sulphuric acid and air, hydrogen peroxide is formed in an amount equivalent to the corroded lead. Traube obtained similar results with zinc in the presence of water. Dunstan, Jowett and Goulding[7] state that "the conclusion is inevitable that, although hydrogen peroxide cannot be actually detected during the rusting of iron, this compound is probably formed as an intermediate product of the change. . . . The conclusion that hydrogen peroxide is formed in the process of rusting receives strong support from the evidence accumulated by other observers that this compound is frequently produced in those chemical changes which involve spontaneous oxidation through the agency of the oxygen of the air.

"The formation of hydrogen peroxide thus appearing to be a necessary part of the chemical process of rusting, the nature of this process required investigation. The formation of hydrogen peroxide during various processes of oxidation has been explained, notably by Hoppe-Seyler in connection with physiological processes, by the supposition that the substance is oxidized by one atom of a molecule of oxygen, the other atom of which attaches itself to a

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[1] Wilson: Ind. Eng. Chem. 15, 129 (1923).

[2] Ber. 15, 2434 (1882).

[3] Z. physik. Chem. 20, 145 (1896).

[4] Bornemann: Z. anorg. Chem. 34, 1 (1903).

[5] "Sixth Report to Corrosion Research Committee of the Institute of Metals." . Inst. Metals, 28, 75 (1922).

[6] Mellor's "Treatise on Inorganic Chemistry," 1, 926 (1922).

[7] J. Chem. Soc. 87, 1548 (1905).

molecule of water forming hydrogen peroxide. Thus in the case of iron the initial change would be

$$Fe+O_2+H_2O=FeO+H_2O_2.$$

"On the other hand, Traube has supposed the oxygen is taken, not from molecular oxygen, but from one molecule of water, the liberated hydrogen combining with a molecule of oxygen to form hydrogen peroxide. Thus, in the case of iron, $Fe+OH_2+O_2=FeO+H_2O_2$, Traube's view involves the assumption that hydrogen peroxide is not oxidised water, but 'reduced' or hydrogenised oxygen, and in support of this contention he has brought forward a considerable body of evidence.

"The two possible modes of formation of hydrogen peroxide have been experimentally investigated so far as they relate to the rusting of iron. Positive evidence has been obtained in support of the theory involving the decomposition of water, whilst negative evidence was forthcoming against the view that oxygen is taken directly from dissolved oxygen. The results distinctly support the conclusion that water is decomposed by the iron and that the liberated hydrogen goes to form hydrogen peroxide with the dissolved molecular oxygen. If the existence of hydrogen peroxide is prevented by the introduction of a soluble substance capable of destroying it, little or no action between the iron and the water takes place at ordinary temperature. The oxidation process appears therefore to be a part of a definite cycle of chemical change, the energy of which is partly derived from the combination of the hydrogen formed. It has been found that rusting of iron can occur in the absence of free oxygen provided that certain oxidising agents are present with which the hydrogen of the water can interact.

"Another possible explanation of the formation of hydrogen peroxide in the rusting process may be noticed here. It has often been suggested that hydrogen peroxide may be formed from oxygen dissolved in water, especially under the influence of light. If this were proved to be the case, the formation of hydrogen peroxide by the direct oxidation of water would be established and an extremely simple explanation afforded of the phenomena of the oxidation of iron. There is, however, no satisfactory recorded evidence that hydrogen peroxide is ever produced in a solution of oxygen in water, whilst rusting commences and proceeds without interruption in the dark."

"If the theory [of Hoppe-Seyler], which supposes direct action of iron on the oxygen is correct, it is probable that the oxygen could be replaced by nitrous oxide which, as is well known, is readily separated into nitrogen and oxygen. The reaction might proceed thus:

$$Fe+ON_2+H_2O=FeO+N_2+H_2O,$$

and rusting should therefore take place in the absence of free oxygen. Two experiments in which pure iron was left in contact with water and nitrous oxide in the absence of free oxygen were carefully carried out in the manner described, but no rusting occurred in either case."

"On the other hand, if it is supposed with Traube that the metal first attacks the water liberating hydrogen, it ought to be possible to replace the oxygen by some reducible substance capable of reacting with the liberated hydrogen. Rusting should then proceed in the absence of free oxygen.

"Experiments were made in which potassium ferricyanide, nitroethane, nitrobenzene, methyl alcohol, free hydroxylamine, and potassium nitrate, respectively, were included in the tube containing pure iron and pure water, the remainder of the tube being full of hydrogen. In order to prove the complete absence of oxygen the hydrogen, before being allowed to enter, was passed through a mixture of pure iron and water only, contained in a tube which was afterwards sealed up; since no rusting took place in this tube, the absence of oxygen was verified. The results of the experiments were as follows: In the case of potassium ferricyanide, the liquid assumed a yellowish-green colour, whilst the surface of the iron became coated with a blue substance; after a time the action ceased and no further change was observed. With nitroethane, ordinary rust was produced on the iron and the liquid became dark in colour. In the case of hydroxylamine, oxidation of the iron occurred and bubbles of gas were evolved. In another experiment in which the iron was exposed to the action of the hydroxlamine and water in a vacuum, the same action was noticed. With potassium nitrate and nitrobenzene, the iron remained quite bright.

"The results of these experiments show therefore that the free oxygen can be replaced by potassium ferricyanide, nitroethane, or hydroxylamine, and that under these conditions rusting of iron takes place in the absence of free oxygen."

Special experiments proved that rusting of iron does not occur at ordinary temperatures "in the presence of either dry or moist oxygen, carbon dioxide, or in a mixture of these gases if the temperature is constant. When, however, the temperature fluctuates and liquid water is deposited on the metal, rusting occurs in the presence of oxygen alone or mixed with carbon dioxide, but not in carbon dioxide alone or in oxygen mixed with ammonia. . . . Experiments were also made in which pure iron and oxygen were left in contact with dry ether instead of water. In this case no rusting occurred. It is therefore concluded from the results of all these experiments that liquid water is essential for the rusting of iron, and that the chemical action involved is the reduction of the water by the iron, the hydrogen thus formed going to produce hydrogen peroxide, which, reacting with ferrous oxide first formed, produces the form of ferric hydroxide known as iron rust."

Dunstan and the others refer to Whitney's electrolytic theory of corrosion but reject it in favor of what they call the hydrogen peroxide theory, apparently not seeing that, if oxygen acts as a depolarizer in an electrolytic cell, hydrogen peroxide must be formed by the reduction of the oxygen. The electrolytic theory of corrosion in presence of air is merely that we have a metal-oxygen cell $M \mid H_2O \mid O_2$. Dunstan himself points out that the free oxygen can be replaced by potassium ferricyanide or nitroethane, which shows that a depolarizer is all that is necessary and that neither oxygen or hydrogen peroxide is essential. It is not clear just how the hydroxylamine functioned. If it acted solely as a reducing agent, it should not have been beneficial and if it was reduced to ammonia, there is no reason why gas bubbles should have been given off. The phenomena described by Dunstan might occur if hydroxylamine lowered the over-voltage for hydrogen; but we do not know that it does that.

While everybody has talked about the depolarizing action of oxygen, it does not seem to have dawned on them that a self-contained electrolytic action involves the existence of a short-circuited voltaic cell. In fact Lambert[1] says that "hydrogen peroxide, which is produced in the wet oxidation of lead, is the product of a subsidiary action, and has no direct bearing on the process of corrosion. It plays a part, however, in oxidizing the monoxide to higher oxides." When a man throws away tricks in this way, it is not surprising that he does not win.

Bengough and Stuart[2] evidently do not understand at all what is meant by a depolarizer. "It appears to be common ground with practically all investigators of corrosion that the presence of oxygen is necessary if any appreciable amount of corrosion of the common metals by water is to take place at the ordinary temperature. There is at present, however, a wide difference of opinion as to the function of oxygen. Its rôle has been explained in two different ways. On one view its function is direct and primary; on the other (and this is a more widely accepted view), its function is considered to be that of a depolarizer, and consequently secondary. These two views may be expressed as follows in the case of a divalent metal:

$$\text{I.}\quad M+H_2O+O \longrightarrow M(OH)_2$$

$$\text{II.}\quad \left\{\begin{array}{ll} M+2H_2O & \longrightarrow M(OH)_2+H_2 \\ H_2+O & \longrightarrow H_2O \end{array}\right\}$$

Reaction I can conceivably take place whether or not a metal can displace hydrogen from solution. Reaction II can only take place if a metal is able to do so."

The second reaction should have been written to show the formation of hydrogen peroxide; but that is a minor matter. The serious error is the statement that Reaction II can only take place in case a metal is able to displace hydrogen from solution. The effect of the depolarizer is to lower the cathode voltage and to make it possible for the reaction to occur at a measurable rate when it could not otherwise do so. Apparently Bengough and Stuart would explain what happens at the cathode in the electrolysis of caustic soda by saying that sodium is first set free and then reacts with water, setting free hydrogen. Potential measurements would have shown Bengough and Stuart that their statement was wrong. This error leads them naturally into another in the next paragraph. "Copper can only displace hydrogen from hot concentrated hydrochloric acid, and then only to a very limited extent. In the case of copper, it is important to notice that hydrochloric and sulphuric acids in the cold will only attack the metal in the presence of oxygen, and there is little

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[1] J. Chem. Soc. **107**, 218 (1915).

[2] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, **28**, 70 (1922).

doubt that the explanation is to be found in the direct oxidation of the copper and the subsequent solution of the oxide."

It is practically certain that this is not the true explanation. If we make up a cell with copper, sulphuric acid, and an oxygen electrode, the copper will corrode readily even though the oxygen is not in contact with it. The ordinary reaction is the same thing in a condensed form and the reaction goes through the hydrogen peroxide stage as shown by Dunstan, Jowett, and Goulding.

Bengough and Stuart[1] wish to limit electrochemical action of cases in which there is a measurable distance between the anode and the cathode; but the advisability of this as a working hypothesis is very doubtful.

"On such a view the electrochemical process (except the colloid precipitation) operated entirely inside the pit, and the process and the result were practically indistinguishable from those associated with the oxidation of the metal; it was merely a question whether or not there was an intermediate and momentary formation of hydrogen—a question that eluded experimental test. In the limiting case in which the anodes and cathodes were indefinitely close together, the difference between chemical and electrochemical action disappeared, and this appeared to be the usual case. In default of evidence the authors preferred the broader term chemical. Subsequent to the initial action, whatever its type might be, corrosion proceeded precisely as on the authors' view. . . .

"It might be pointed out that in certain cases electrochemical action became indistinguishable. Thus if hydrogen were being displaced by a metal in acid, and the hydrogen were being evolved uniformly as far as even microscopic observation could ascertain, then there was no means of distinguishing between spatial separation and contact between the reacting bodies, since any cathodes and anodes must be indefinitely close. The authors, therefore, preferred to distinguish as electrochemical those cases in which a perfectly clear distinction could be made between the cathodes and anodes. It might be noted that the adherents of the electrochemical view of corrosion claimed that such distinction would be readily made by means of the ferroxyl test."

This seems to explain what is otherwise a meaningless paragraph.[1] "The oft-repeated general statement, that metals of a high degree of commercial purity are less readily corroded by neutral media than more impure metals (a statement that is usually put forward as a proof that corrosion is electrochemical, though it is also explainable on other grounds), can only be accepted with great reservations. It is true that Ramsay and Reynolds' highly purified zinc was only slightly attacked by acid, unless a trace of platinum black was added to it. The platinum may, however, have affected the rate of corrosion by facilitating the chemical evolution of hydrogen at the surface of the metal owing to the lowered over-voltage rather than by the formation of a couple."

These two things are identical and not antagonistic as Bengough and Stuart would have us believe. The platinum acts by forming a couple which

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[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 128 (1922).

[1] Bengough and Stuart: "Sixth Report to the Corrosion Research Committee of the Institute of Metals," J. Inst. Metals, 28, 59 (1922).

permits the evolution of hydrogen at the platinum cathode because of the low over-voltage there.

The proof of the pudding is in the eating. The Sixth Report does not incline one to accept the views of Bengough and Stuart. Some experiments on the action of metals on nitric acid are now being carried on at Cornell. When these are finished, there will be available some very interesting evidence of the effectiveness of the electrolytic theory of corrosion as a working hypothesis. Bengough and Stuart will scarcely claim that the consideration of this problem as a purely chemical one has been successful in giving us a satisfactory theory of the phenomena.

Dunstan, Jowett, and Goulding[1] made some experiments to determine what metals gave hydrogen peroxide when corroding in presence of oxygen. "The action of oxygen and water on several metals in the presence of a trace of sulphuric acid, which would promote the liberation of hydrogen, was now examined in the following manner. The metal was placed under distilled water containing a trace of sulphuric acid, and oxygen was bubbled through the liquid for some time. The mixture was then shaken and tested for hydrogen peroxide from time to time. It was found in all these instances except in that of iron. A parallel series of experiments was carried out omitting the sulphuric acid, and, except in the case of zinc, no hydrogen peroxide could be detected.

The results of the experiments made in the presence of acids were as follows:

Metal.	*Result.*
Copper.	After 48 hours, the liquid was of a faint blue colour, and gave a distinct reaction for hydrogen peroxide.
Mercury.	After 2 hours, a distinct reaction for hydrogen peroxide.
Silver.	After 24 hours, a trace of hydrogen peroxide was found.
Lead.	The liquid became milky at once, and gave a well-marked reaction for hydrogen peroxide.
Bismuth.	A well-marked reaction for hydrogen peroxide.
Tin.	The reaction was not so well marked as in the case of bismuth.
Zinc.	A well-marked reaction for hydrogen peroxide.
Iron.	Although examined from time to time, no hydrogen peroxide could be detected.

"Thus, hydrogen peroxide was found in every case except in that of iron. If hydrogen peroxide were produced in presence of iron, it would be at once decomposed.

"In order to ascertain whether hydrogen peroxide would attack iron in the presence of a substance which inhibits ordinary rusting, metallic iron was introduced into solutions of borax and lime respectively, and hydrogen peroxide was then added. The iron in these cases remained unattacked although the peroxide was decomposed and oxygen was evolved. If a plate of bright and highly polished steel is immersed in a strongly alkaline solution of hydrogen peroxide, decomposition of the hydrogen peroxide is extremely rapid and

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[1] J. Chem. Soc. 87, 1560 (1905).

bubbles of oxygen are liberated on the surface of the steel, yet no rusting occurs if the alkaline solution is fairly strong."

All this is grist to the electrolytic mill and this is not the only slip that Dunstan, Jowett, and Goulding made. One of their reasons for rejecting the electrolytic theory of corrosion was that it would not account for the fact that potassium bichromate solution prevents the rusting of iron. Bengough and Stuart[1] make much of the same fact. "The action of bichromate solutions in passivifying metals is not readily explained on electrochemical lines, since bichromate is a powerful depolarizer, and would be expected greatly to enhance any electrochemical action that took place in distilled water (as indeed it does in certain acid solutions). . . . An interesting point arises in connection with the function of known depolarizers, such as potassium bichromate. In electrochemical corrosion, as, for instance, in the case of the primaries, these substances powerfully promote corrosion of the anode. But when metals such as iron, zinc, and copper, and even magnesium, are placed in distilled water containing bichromate, corrosion is inhibited." Evans[2] has objected to the second part of the quotation as misleading because the bichromate is not added in contact with the corroding metal in the primary cell whereas it is in the corrosion experiments. "It was true that the presence of chromates at the cathodic portions of the corrosion couples would be favorable to the reaction; but at the anodic portions they would stop the reaction altogether. Since the cathodic action could not proceed without the anodic action, corrosion would cease. Many workers had shown that if an electrolytic cell fitted with an iron anode dipping in a neutral non-oxidizing salt solution were joined to an external battery iron was dissolved at the anode; but the addition of a little chromate to the solution stopped the anodic dissolution of the iron altogether.

To this comment the only reply that Bengough and Stuart made, (p. 127), was that "the writers had been very interested in Mr. Evans' explanation of the behaviour of bichromate in inhibiting corrosion. He suggested that it was a case of anodic polarization produced by the formation on the anodic surface of some form of oxide. But surely this was a case of direct oxidation such as was postulated all along by the authors."

Unfortunately, Bengough and Stuart did not explain what they meant by their last sentence. As a matter of fact we shall see that Bengough and Stuart were wrong and that Evans was right. It would have been interesting if Evans had carried the war into Africa and had pointed out that bichromate is not a strong depolarizer at the concentrations used in the corrosion experiments.

One would think, to read the comments by Bengough and Stuart, that the upholders of the electrolytic theory of corrosion either knew nothing about the action of bichromate or avoided all mention of the painful fact. Nothing

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[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." Jour. Inst. Metals, 28, 52, 74 (1922).

[2] Discussion of "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 129 (1922).

could be further from the truth. Cushman and Gardner[1] pointed out that "as has already been noted, solutions of chromic acid and potassium bichromate inhibit the rusting of iron. In order to determine the concentration necessary to produce complete protection, a number of polished strips of two different samples of steel were immersed in bichromate solutions of increasing concentration, contained in tubes which were left quite open to the air. There were twelve tubes in each series, ranging by regular dilutions from tenth-normal down to ten-thousandth normal. At the end of two months the last four tubes showed graded rusting with accumulations of ferric hydroxide. No rusting had occurred in any of the solutions above tube No. 8, which contained six-hundred-and-fortieth normal bichromate, a strength corresponding to about 8 parts of the salt in 100,000 parts of water, or about 2 pounds to 3,000 gallons. Since solutions of bichromate do not hydrolyze with an alkaline reaction, but on the contrary are usually slightly acid, some other explanation must be found for this remarkable phenomenon. On first thought it would seem a paradox that a strong oxidizing agent should have the effect of preventing the oxidation of iron, and yet this is precisely the case. If, however, the initial cause of rusting is the hydrogen ion, it is possible to believe that under certain conditions oxygen would prove the most effctive inhibitors.

"One of the authors has observed that, if a rod or strip of bright iron or steel is immersed for a few hours in a strong (5 to 10 percent) solution of potassium bichromate, and is then removed and thoroughly washed, a certain change has been produced on the surface of the metal. The surface may be thoroughly washed and wiped with a clean cloth without disturbing this new surface condition. No visible change has been effected, for the polished surfaces examined under the microscope appear to be untouched. If, however, the polished strips are immersed in water it will be found that rusting is inhibited. An ordinary, untreated, polished specimen of steel will show rusting in a few minutes when immersed in the ordinary distilled water of the laboratory. Chromated specimens will stand immersion for varying lengths of time before rust appears, but the induced passivity gradually disappears.

"The passivity which iron has acquired can be much more strikingly shown, however, than by the rusting effect produced by air and water. If a piece of polished steel is dipped into a one percent solution of copper sulphate, a 10-second immersion is sufficient to plate it with a distinctly visible coating of copper which cannot be wiped off[2]. A similar polished strip of steel which has been soaked over night in a concentrated solution of bichromate and subsequently well washed and wiped will stand from six to ten 10-second immersions in 1 percent copper sulphate before a permanent coating of copper is deposited. Even a momentary plunging of the metal into the bichromate will induce a certain passivity, but the maximum effect appears to require a more prolonged contact with the solution. . . . It has been already pointed out in a previous chapter that in many cases a stimulative

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[1] "Corrosion and Preservation of Iron and Steel", 111 (1910).

[2] This experiment has failed in hands of certain experimenters who have not been careful to use the copper sulphate solution as dilute as directed.

and an inhibitive tendency may be at work at one and the same time. This assertion is well brought out by the following experiment in which an inhibitoi and stimulator are literally 'pitted' against one another. Samples of bright steel wire were immersed in 100 cubic centimeters of a very dilute one-thousandth normal solution of potassium bichromate in a series of shallow dishes. The wire test pieces were suspended in the solution so that they did not come in direct contact with the glass surfaces of the dishes. This precaution should never be omitted in experiments of this kind, as owing to the absorption of air by glass, rusting is always stimulated at the point of contact between glass and iron. The first dish was left as a blank, the second received one drop equal to 1/20 cubic centimeter of a dilute tenth normal copper sulphate solution. The third dish received two drops of the solution, and so on, each dish getting an increased amount of copper sulphate until twenty-five dishes had been prepared.

"Now it is apparent that we have in this system two contending forces at work. Iron has a higher solution tension than copper, and therefore tends to pass into solution, the copper tending to plate out on the iron. Chromate ions, on the other hand, put the surface of iron in a condition in which it cannot pass into solution. In the solution system iron-chromate-copper we have an equilibrium to be decided between two contending forces acting in opposite directions. It was interesting and instructive to note the results of this struggle, which was known to be going on, although the actual conflict could not be watched. In the first dish, in which no copper was present, no corrosion took place; in the second, also, no action was visible; in the third, however, minute specks of iron rust appeared. These were larger and more frequent in the immediately succeeding dishes, the test-pieces showing rust tuberculation with the well-known pitting effect. As the middle of the series of dishes was approached, both iron rust and precipitated copper began to appear side by side on the surface of the iron, and from thereon in the series more and more copper separated, while less and less rust formed, until in the end dishes copper and iron were changing places evenly over the surface without apparent hindrance. These experiments, and other of a similar nature, were repeated many times with the same results, and there seems to be no escape from at least the following two conclusions to which they obviously lead:

"(1) If the surface of iron is subject to the action of two contending influences, one tending to stimulate corrosion and the other to inhibit it, the result will be a breaking down of the defensive action of the inhibitor at the weakest points, thus localizing the action and leading to pitting effects.

"(2) While the concentration of an inhibitor may be strong enough to prevent the electrolyte exchange between atom and ion, it must be still stronger to prevent entirely the solution of iron and the subsequent oxidation which leads to the formation of rust-spots."

Dunstan and Hill[1] state that all agents which inhibit rusting render passive the metals studied by them. Among the solutions acting in this way was a one percent solution of potassium bichromate. This was checked qualitatively

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[1] J. Chem. Soc. 99, 1835, 1855 (1911).

by Miss Souders[1] at Cornell who suspended strips of magnesium, zinc, iron, and copper in a bichromate solution for several weeks. The surfaces of all these metals remained practically untarnished. If the electrolytic theory of corrosion is correct, this should mean that these metals would not undergo corrosion when made anode in a bichromate solution under suitable conditions. The solution used in the electrolytic experiments was M/40 $K_2Cr_2O_7$ which is a little less than one percent. Voltage current curves were determined for the cell M | K_2 Cr_2O_7 | Pt. With iron there was visible evolution of oxygen and hydrogen at 2.2 volts and the decomposition voltage was found by extrapolation to be about 2.0 volts. The evolution of hydrogen at the cathode shows that potassium bichromate is not a powerful depolarizer at this concentration. The hydrogen was not determined experimentally, so we cannot say definitely that there was no depolarization; but the curve was absolutely normal in every respect so it seems that the amount of hydrogen oxidized was negligible. This matter is now under investigation at Cornell. The iron anode did not corrode perceptibly, so there is perfect agreement between the ordinary and the electrochemical phenomena. In order to study the effect of the addition of sodium chloride, varying amounts of M/40 NaCl solution were substituted for the M/40 $K_2Cr_2O_7$ solution. The decomposition voltage decreased with increasing relative amounts of sodium chloride and the corrosion of the anode also increased. The iron anode did not corrode perceptibly in the solution containing 99 parts bichromate to one of salt and the form of the decomposition voltage curve changed but slightly. With 75 parts bichromate to 25 parts salt, the decomposition voltage is roughly 0.5 volts by extrapolation. No experiments were made with a bichromate solution diluted with water alone; but a whole series of experiments is planned for different concentrations and temperatures. In order to compare the anodic corrosion with ordinary corrosion, strips of iron were immersed in solutions identical with those used in the decomposition-voltage experiments. At the end of a week the iron had corroded in all the mixtures except the one containing 99 parts bichromate and one part of salt, and the amount of corrosion varied directly with the concentration of the sodium chloride.

Copper, zinc and magnesium corroded when made anodes in the potassium bichromate solution, which was distinctly not according to Hoyle. It was noticed, however, that the cell Cu | K_2 Cr_2O_7 | Pt had an electromotive force of approximately 0.3 volts when measured on open circuit with a potentiometer; but no current flowed when the cell was short-circuited on a milliammeter. No corrosion took place when a platinum wire was wrapped tightly round a copper wire and the whole was immersed in a bichromate solution, while marked tarnishing was perceptible in a few hours when a similar pair of wires was immersed in a M/40 Na_2SO_4 solution. This showed that copper became passive for low current densities and active when a sufficient voltage was impressed.

Miss Souders measured the anode potentials of iron, copper, zinc and magnesium in M/40 $K_2Cr_2O_7$ at the decomposition point and found that they

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[1] Unpublished thesis.

were all much more noble than they should be. The actual data will be published some day in her thesis. At low voltages, which is what we deal with in corrosion experiments, the ordinary and electrolytic corrosions run parallel; but the passivity breaks down at higher voltages for copper, zinc, and magnesium, just as it breaks down in the aluminum rectifier though the phenomenon is much more striking in the latter case. The difficulties imagined by Bengough and Stuart have vanished into thin air and we see that Evans was right in saying that the anode reaction was the important one in these cases.

Alkalies are also inhibitors of corrosion; but the explanation of this action given by Cushman and Gardner,[1] Walker, and others is inadequate. "All substances in solution which contain hydrogen ions, such as acids, stimulate the corrosion of iron. This is also true of salts of strong acids and weak bases, which, though perfectly stable in a dry condition, hydrolyze in solution to an acid reaction; or which, though neutral in fresh solutions, undergo slow decomposition under the action of light, with the formation of acid salts or free acid. With certain exceptions, salts which are perfectly neutral in solution do not prevent oxidation but appear to aid it by increasing the electrolytic action. All substances which develop hydroxyl ions in solution, such as the alkalies or salts of strong bases with weak acids, to a certain extent inhibit, and, if the concentration is high enough, absolutely prohibit, the rusting of iron.[2]

"Under the electrolytic theory the explanation of the protection afforded by hydroxyl ions is a simple one. Owing to the small dissociation of water, hydrogen ions cannot exist in a solution in which the hydroxyl ions are in excess.[3] As hydrogen ions cannot exist or be locally formed in sufficiently strong alkline solutions, no attack is made upon the iron, which remains permanently unaltered. If, however, the concentration of the hydroxyl ions is not sufficiently great, electrolysis can go on with an apparent stimulation of the pitting effects similar to that produced by perfectly neutral electrolytes, such as sodium chloride."

This view is not consistent with the later generalization of Dunstan and Hill that all substances which inhibit rusting render the metal passive. Miss Souders finds that with increasing anodic polarization of zinc in a one percent caustic soda solution, the zinc is first active, then passive, and finally active again. In a sodium chloride solution there is of course no evidence of passivity; but marked evidence of passivity is to be seen with a 0.9% NaCl+0.1% NaOH solution and the curve for 0.5% NaCl+0.5% NaOH does not differ appreciably from that for 1% NaOH. An iron anode polarizes in 1% NaOH to practically the same value as in M/40 $K_2Cr_2O_7$, about 0.7-0.8 volts cathodic when the hydrogen electrode is taken as zero. Zinc is less noble in caustic

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[1] "Corrosion and Preservation of Iron and Steel," 110 (1910).

[2] Under exceptional conditions this statement may require modification. Iron has a considerable solution tension in strong boiling alkaline solutions; but in such a case the equilibrium is reversed and the metal acts the part of a negative radical in conjunction with oxygen. This point is at present being investigated.

[3] [Cushman did not say exactly what he meant, which is that hydrogen ions cannot occur except in very low concentration.]

soda than in bichromate, while copper and magnesium are much more noble when polarized anodically in caustic soda than in bichromate.

Bengough and Stuart[1] are quite impressed with their observations on corrosion in distilled water and in sea-water. "Support for the view that the course of corrosion is not always determined by the conductivity of a solution can easily be found, however, even in acknowledged electrolytes. Thus metallic zinc is corroded from four to six times as rapidly by stagnant distilled water, as by sea-water or 2.5 percent sodium chloride, both of which are excellent electrolytes. Nickel and lead are also more rapidly corroded in stagnant distilled water than in sea-water. It is clear, therefore, that the conductivity of the corroding liquid may be quite a minor factor in many corrosion phenomena, whereas the nature of the scale may be a major factor. . . .

"This statement [in regard to over-voltage], however, does not take into account certain relevant experimental facts which are that distilled water will readily corrode zinc, even when highly purified, and no hydrogen is evolved; 2.5 percent sodium chloride solution when stagnant, will only attack the same sample of zinc much less slowly; extremely dilute weak acid, such as acetic acid, will also attack it readily, but with quantitative evolution of hydrogen. It follows from these facts that neither the over-voltage nor the depolarization of hydrogen by atmospheric oxygen have any important effect on the result, since the former is not able to stop corrosion and the latter cannot assist it. The important facts determining the rate of corrosion are of quite another kind. Over-voltage phenomena, in fact, afford little assistance in elucidating corrosion by water and salt solutions, except in those comparatively few cases in which hydrogen is displaced from solution, *e.g.* by magnesium from sodium chloride solutions."

Only reckless men would draw any conclusions from experiments on the corrosion of zinc in distilled water and in sodium chloride solution. Miss Souders made some experiments with (1) aerated distilled water, (2) aerated sodium chloride solution, (3) stagnant distilled water, and (4) stagnant sodium chloride solution. At the end of five days the order of corrosion from highest to lowest was: aerated sodium chloride; aerated distilled water; stagnant water; stagnant sodium chloride. At the end of fifty days the order was stagnant sodium chloride; aerated sodium chloride; aerated distilled water; stagnant distilled water. In all cases a film forms and at the end of fifty days the corrosion ceased practically in the cases of aerated sodium chloride, aerated water, and stagnant water, even if one substituted fresh liquid. The stagnant sodium chloride was not carried to an end; but it looked at the end of eighty-five days as though the corrosion were nearly ended. The amount of corrosion depends on the way in which the film forms and that is probably a function of many factors, many of them probably almost insignificant ones. I offer no explanation why the stagnant sodium chloride did so much better than any of the others; but I do feel that data like these should not be put forward seriously as proving anything.

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[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 53, 80 (1922).

Another phenomenon which seems convincing to Bengough and Stuart[1] is the behavior of magnesium. "A very formidable difficulty in the way of the electrochemical theory of corrosion is found in the effect of ions of the corroded metal on the rate of corrosion of a liquid containing them. The presence of these ions, in the case of such metals as magnesium, zinc, aluminum, iron, nickel, and tin, should decrease the rate of corrosion according to the theory, by increasing the osmotic pressure which opposes the solution tension. It has, however, long been known that magnesium chloride is an extremely powerful corrosive agent for magnesium,[2] far more so than distilled water or the chlorides of the alkaline earths or heavy metals, and hydrogen is freely evolved from the metal and does not protect it at all. Dhar[3] has shown that the presence in solution of the ions of the corresponding metal increases the potential difference between the metal and water of a neutral salt solution instead of lessening it, as required by the theory in the cases of magnesium, aluminum, zinc, and iron; nickel and tin, on the other hand, show a decreased potential difference."

Since magnesium cannot be precipitated from an aqueous solution, a magnesium electrode in an aqueous solution of a magnesium salt is not a reversible equilibrium and one cannot apply the Nernst theory to it. This is the same sort of mistake that Carhart[4] made over twenty years ago when he wished to consider nickel in nickel sulphate solution as a reversible electrode. This is, however, a minor matter and the really important thing is why magnesium corrodes more rapidly in a magnesium chloride solution than in distilled water. There is fortunately no dispute in regard to the facts.

The explanation was suggested by Bryant[5] the same year that Tommasi published his experiments. Bryant studied the action of alcohol, water, and sodium sulphate upon magnesium and found that the rate of reaction increased from alcohol to sodium sulphate. "Magnesium has itself, I submit, the power to decompose water at all temperatures above 0°C, and the action is stopped by an insoluble coating of oxide forming in the metal. This would explain the change of color seen after the action has ceased, the renewal of action when the surface is cleaned, and the abundant evolution of gas from a solution of sodium sulphate, since magnesium oxide is more soluble in that than in pure water." If Bryant had only known the magic word, peptization, he could have explained everything.

Miss Souders immersed two rods of magnesium, each 10 cm long and 1 cm in diameter, in pure water and in one percent magnesium chloride solution respectively. The rod in the magnesium chloride solution became covered with white flakes[6] which were easily removed; the solution was milky, and

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[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 61 (1922).

[2] Tommasi: Bull. 21, 885 (1899); Kahlenberg: J. Am. Chem. Soc. 25, 380; Roberts and Brown: 841 (1903); Getman: 38, 2596 (1916); 39, 596 (1917).

[3] Z. anorg. Chem. 118, 75 (1921).

[4] Trans. Am. Electrochem. Soc. 1, 105; 2, 122 (1922).

[5] Chem. News, 80, 211 (1899).

[6] Cf. Evans: J. Inst. Metals, 28, 117 (1922).

a considerable precipitate settled to the bottom. The rod which had been in the water acquired a dull lusterless surface which was moderately smooth; the liquid was clear. The rods were then transposed, the one that had been in the water being placed in the magnesium chloride solution, and the one that had been in the magnesium chloride solution being placed in the water. The rod which was now in the magnesium chloride solution began to flake and become rougher, the film originally produced by the water being obliterated entirely. The rod which had been transferred to the water became more like the one which had started in the water, the surface seeming smoother and the coating more adherent. It never got really back because the original pitting had been too severe. There is no question, however, but that the two films are quite characteristic and that the film in water retards corrosion. For this discussion it is immaterial whether one says that magnesium chloride peptizes magnesium oxide or not. That is the simplest explanation because we know that zinc chloride peptizes zinc oxide, ferric chloride peptizes ferric oxide, and chromic chloride peptizes chromic oxide. The essential thing is that there is nothing mysterious about the corrosion of magnesium in a magnesium chloride solution. Any sceptic can repeat the experiments and satisfy himself.

One reason why Bengough and Stuart[1] have considered corrosion experiments in distilled water so important is that they believe that the conductance of the liquid medium should be a very important factor in determining the rate of corrosion. They say that a fact which is "difficult to explain on a purely electrochemical theory" is that "the conductivity of electrolytes is not directly connected with the amount of corrosion." There is some justification for this attitude. Walker[2] stated that "the third factor [influencing the rate of corrosion] is the ease, due to the lack of resistance, with which the electric current, generated by the solution of the metal at one point and the separation of the molecular hydrogen at another, can pass from one of these points to the other. They may be infinitely close together, or separated by quite a distance. Therefore, this theory demands that solution or corrosion should take place more rapidly in water in which there is dissolved a trace of an electrolyte, than in absolutely pure water."

Taken by itself, this paragraph might seem to support the contention of Messrs. Bengough and Stuart; but this is one of the statements that everybody understands to mean that the rate of corrosion increases with the conductance provided other things remain equal—which they rarely do. In the preceding paragraph Walker had mentioned that caustic soda inhibits the corrosion of iron and that he had shown the inadequacy of Friend's experiments by showing the presence of caustic soda on the iron by means of conductance experiments. Walker[3] has covered the case explicitly himself in a later paper. The factors which influence corrosion are: "third, the ease with

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[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 32 (1922).

[2] Trans. Am. Electrochem, Soc. 14, 178 (1908).

[3] Trans. Am. Electrochem. Soc. 29, 436 (1916).

which the hydrogen ion reaches the iron. For example, the wonderful resistance of sheet steel containing small quantities of copper is unquestionably due to the adherent nature of the film of oxide produced when corrosion starts. This film, as in the case of the alumina coat on metallic aluminum, effectually insulates the metal and practically prevents further corrosion."

This seems to be an appropriate time to introduce two quotations from W. D. Richardson,[1] just to show that people have recognized the existence of factors which would modify the conclusions which one might draw from the electrolytic theory of corrosion in its simplest form.

"The solution tension of a metal which determines its position in the electrochemical series, one might suppose would be a dominant factor in determining the rate of solution in an acid, as well as the rate of corrosion. Abundant evidence shows that it does neither of these things. It represents only a tendency to go into solution, a tendency which under the ordinary conditions of the experiment is so quickly brought to a halt by various influences, on the other hand so readily accelerated by catalysts, and so seldom realized, that the actual order of corrodibility and solution of metals is quite at variance with the order in the electrochemical series. It is so easily overbalanced by polarization with hydrogen, by the influence of oxygen with or without the resultant formation of a passive layer, by the effects of impurities in the metal, and by the influence of the products of corrosion, that it is rarely the determining factor."

"Matters do not occur according to the simple idea or the simple conception of the electrolytic theory of corrosion as advanced in the early days, and that is what I meant when I spoke of the older view of it. The recent view, and it is coming more and more into prominence, is that while this older view of a simple electrolytic theory is at the basis of all corrosion phenomena, there are so many modifying, upsetting and antagonizing influences that it does not take a straight course as we might expect if we had no further knowledge of it. Let me call your attention to one upsetting influence, rust, which I have emphasized over and over again, may accelerate in a general way, the corrosion of iron. If it forms a closely adherent layer of the physical nature of a paint film over the entire surface, it may stop corrosion by preventing the access of water and oxygen, and if it is entirely adherent in patches, it may cause deep pitting. Now here we have the same general influence acting in different ways, in all instances upsetting the ordinary action of the corrosive substances and elements."

"I believe we have another influence to contend with which may act in different and antagonistic ways, namely oxygen. We know that oxygen is the chief disturbing influence in ordinary corrosion; it is the principal substance which causes corrosion to go in some other way than we might expect from the simple theory. We know that the corrosion of iron goes on at practically the zero rate in the absence of oxygen and in the presence of water, and we know it may go on very rapidly in the presence of pure oxygen and less rapidly in air. We know, too, that the influence of oxygen or an oxidizing agent on the

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[1] Trans. Am. Electrochem. Soc. 38, 248 (1920); 39, 162 (1921).

surface of iron may be such as to produce the passive condition, and when this condition supervenes, the iron behaves as monel metal and there is no corrosion at all. I have been led to suspect by some phenomena, that I have mentioned in an earlier paper in connection with some work on cast iron, that a modified passivity may supervene in instances where we have not suspected it. I do not know that this theory explains it, but in the case of cast iron we have some very peculiar rust-resisting properties, and it may be under certain conditions the iron coupled with graphitic carbon and under oxidizing conditions may assume, temporarily at least, or from time to time, or intermittently, a passive condition. In discussion with Dr. Burgess last evening on the subject of copper steel, I spoke with him about the experiments which I had made, adding copper to normal nitric acid, with the result that the corrosion rate was lower, and he suggested that possibly in that case passivity was induced. I then spoke to him about the effect of graphitic carbon or cast iron, and it may be that in the case of the copper steel, we have an induced passivity, or intermittent passivity, which may account for the action of copper in that instance. I think none of us can afford to be at all dogmatic in our discussions of corrosion, and particularly when we are dealing with a metal like copper of proved peculiar behavior."

At the risk of appearing dogmatic, it seems that Bengough and Stuart[1] are still living in the era of Cushman and Lambert, besides being handicapped by a very rudimentary knowledge of electrochemistry. "If gold be placed in a beaker of chlorine water it will be slowly attacked, and pass into solution forming gold chloride. Since gold cannot displace hydrogen from water or hydrochloric acid, and is not attacked by the chlorine ions existing in such easily reducible solutions as cupric chloride, it is reasonable to assume that the reaction is not ionic but molecular and that the non-ionized chlorine molecule which exists in the chlorine water directly attacks the gold.

$$2\,Au+3Cl_2 \longrightarrow 2CuCl_3 \text{ liq.}(+54338 \text{ cal.}).$$

This view of the action is suggested by the position of gold and chlorine in the electrochemical series; they occur together at one end, and would therefore tend to combine by virtue of their non-ionized valencies rather than by their ionized valencies. The fact that the resulting solution of the gold contains complex ions such as $(AuCl_3O)''$ in water, and $(AuCl_4)'$ in dilute hydrochloric acid also suggests that the initially formed molecular compound does not entirely rearrange itself so as to form the simple $Au^{\cdot\cdot\cdot}$ and Cl' ions, which would be expected from the ionic formation of $AuCl_3$.

"Thus, it seems reasonable to assume that the gold has passed into solution by purely chemical action. It is possible, however, to arrange that the gold shall pass into solution electrochemically. If the chlorine water be replaced by sodium chloride solution, no gold will dissolve; but if the gold be electrically connected to a piece of platinum placed in another beaker containing sodium chloride, and the two beakers be connected by a siphon and chlorine water be poured over *the platinum*, then the gold will dissolve and a

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[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 44 (1922).

current will pass. The action is now carried out electrochemically, since there is spatial separation of the reacting bodies and free energy has appeared as an electric current. Gold has been oxidized at the anode, thus:

$$2\,Au \longrightarrow 2\,Au^{\cdot\cdot\cdot},$$

and the chlorine has been reduced at the cathode thus:

$$Cl_2 \longrightarrow 2\,Cl'$$

A similar result has been reached as in the chemical process, by a different route and at a different speed.

"A similar series of experiments could be carried out with platinum and it seems fair to assume that certain metals, at any rate, may be corroded either chemically or electrochemically, and that the actual conditions of the experiments might determine in which way the action would proceed."

Bengough and Stuart have been fair in admitting explicitly that it is only an assumption that gold reacts chemically with chlorine under these circumstances. What their experiments prove is that gold can react with chlorine electrochemically and that the same reaction takes place when there is no spatial separation. If one is to assume, as they do, that the whole type of reaction changes when the anodes and cathodes are very close together, one would like to know at what point the change in type occurs. It is quite possible that Bengough and Stuart would say that the change came when the chlorine was in contact with the gold and not with the platinum; but that will not do, because the same results would have been obtained with a gold cathode provided the resistance of the circuit was kept low enough.

There is nothing to show whether they italicized the words "the platinum", because they were surprised that the chlorine should be added there or because they thought that their readers would be surprised; but there seems to be no justification for either thing because the general principle was explained in detail by Ostwald[1] over thirty years ago.

"As is well-known, amalgated zinc is not attacked by dilute acids, but it dissolves in acid with evolution of hydrogen if a piece of platinum wire is wrapped round the zinc. Zinc wrapped with platinum does not dissolve in solutions of neutral salts but does if a few drops of acid, sulphuric acid for instance, be added to the salt solution. For the platinum to have this effect it is only necessary for it to be in contact with the zinc at a single point. If one makes a staple out of zinc and platinum with the two ends only a little way apart and dips this into potassium sulphate solution so that a diaphragm of porous material, such as earthenware or parchment paper, separates the two ends, it is a simple matter to determine which of the metals, zinc or platinum, must come in contact with the acid in order to make the zinc corrode.

"At first sight, the question seems absurd; for if the zinc is to corrode, it seems self-evident that the acid should be added to it. If one tries the thing out, however, the opposite proves to be true. When one adds acid to the potassium sulphate solution in contact with the zinc, no zinc dissolves except traces which would have gone into solution anyhow; it dissolves rapidly and there is a plentiful evolution of hydrogen when the liquid round the platinum

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[1] Z. physik. Chem. 9, 540 (1892).

is made acid. The hydrogen comes off at the platinum as is always the case when zinc is in contact with platinum. In order to dissolve zinc under these conditions, it is therefore necessary to add the attacking substance to the platinum which is connected with the zinc and not directly to the zinc which is to be attacked."

Bengough and Stuart state that it is reasonable to assume "that the non-ionized chlorine molecule which exists in the chlorine water directly attacks the gold." They have evidently forgotten that Wohlwill[1] has shown that a gold anode does not corrode in a neutral auric chloride solution or in a solution of chlorauric acid, $HAuCl_4$. Chlorine is evolved at the anode, which seems to dispose pretty effectually of the assumption that chlorine reacts direct with massive gold. The anode does corrode when there is an excess of hydrochloric acid so that chlorauric acid can be formed. While Bengough and Stuart are quite right in saying that gold cannot react with hydrochloric acid, displacing hydrogen, they have overlooked entirely the fact that gold can and does react with hydrochloric acid when chlorine is present as a depolarizer. Just as the corrosion or non-corrosion of iron in presence of oxygen is to be considered as the action of a cell, Fe | solution | O_2, so the corrosion is to be considered as the action of a cell, Au | HCl | Cl_2.

Coehn and Jacobsen[2] have studied the anodic behavior of gold in gold chloride and in hydrochloric acid solutions and find that the gold anode becomes passive at current densities which become higher as the concentration of hydrochloric acid increases.

Bengough and Stuart[3] devote nearly six pages to the behavior of copper electrodes in sodium chloride and cupric chloride solutions, so they presumably consider these experiments as significant. They placed a half-normal cupric chloride solution inside a porous cup and a three percent sodium chloride solution outside. In these two solutions they placed two similarly shaped copper electrodes (99.96 percent copper) and connected them metallically so as to form a concentration cell, the electrode in the sodium chloride solution being of course the anode and the one in the cupric chloride solution the cathode. At the end of twenty-four hours, the electrodes were removed, examined, dipped momentarily into strong hydrochloric acid to remove cuprous chloride, and then weighed. The anode lost 6.93 grams and the cathode had gained half a gram which they saw as crystals of copper. They do not realize that this is conclusive proof of bad experimentation. Under the conditions which they describe and thought they had, no copper could precipitate on the cathode until practically all of the cupric chloride had been reduced to cuprous chloride and that they say was not the case. It is quite clear that a film of cuprous chloride formed over the cathode and that for a portion of the time no cupric chloride was in contact with the cathode.

At the time when they started the electrolytic experiment, they also placed similar pieces of copper, not electrically connected, in each of the solutions.

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[1] Z. Elektrochem. 4, 381 (1898).

[2] Z. anorg. Chem. 55, 330 (1907).

[3] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 45 (1922).

At the end of the twenty-four hours the results were just what everybody would have predicted, a thin film of cuprous chloride on the piece of copper in the sodium chloride solution and a thick film of cuprous chloride on the piece of copper in the cupric chloride solution. After being cleaned, the copper in the sodium chloride solution had lost 0.13 grams and the one in the cupric chloride solution 3.0 grams.

Most people would consider the reaction between copper and a cupric chloride solution as essentially electrolytic; but not so Bengough and Stuart. Having assumed that the corrosion of copper in a cupric chloride solution is chemical, partly because no current is generated and partly because the corrosion is fairly uniform over the surface of the copper, they say that "it seems fair to draw the conclusion that if copper is to be corroded electrochemically without the existence of an external electromotive force, it must either not be placed in the cupric chloride at all, or else it must be so placed that a concentration cell effect may be produced. If it be placed in a homogeneous solution of cupric chloride, so that the essential condition of chemical action, namely, contact, be fulfilled, then it may be predicted that it will be initially corroded chemically, and energy will be set free as heat, since the action is exothermic. If the reaction products be not uniformly distributed, concentration cells may arise in course of time. From these experiments, it is clear that a metal can be corroded either chemically or electrochemically according to the conditions prevailing in its neighbourhood—*conditions which are independent of the metal itself*. When conditions specially favour the electrochemical type, the action may be more rapid than with the chemical type; when, however, they do not, then the chemical action may be more vigorous. For instance, if a considerable resistance be introduced into either or both of the conducting circuits, then the electrochemical action may be reduced approximately to zero."

The experiments prove nothing in regard to the chemical corrosion of copper. It was assumed that the corrosion of copper in cupric chloride solutions is chemical corrosion. If one is to assume that, there is no point in the experiments because everybody admits that metals can be corroded electrolytically. The only point worth noticing is that the electrolytic and the so-called chemical corrosions give identical products when the experiments are done carefully, though not when done by Bengough and Stuart. A point of view which does not enable one to detect obvious errors does not have much pragmatic value as a working hypothesis.

After this unfortunate episode with cupric chloride Bengough and Stuart[1] say that "many other cases might be quoted which are difficult or impossible of explanation on the assumption that no direct chemical action can take place between the metal and the liquid in which it is placed; only two or three will be mentioned. Thus, if copper be electrically connected with aluminum in nitric acid (1 of acid: 3 of water) the electromotive force of the couple is about 0.47 volt, the aluminum being the anode and the copper the cathode. Never-

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[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 51 (1922).

theless, the copper rapidly reduces the nitric acid in its neighbourhood and passes into solution with solution of oxides of nitrogen. The aluminum is also slightly, but much less attacked. In such circumstances it seems clear that the nitric acid is chemically reduced by the copper, which is simultaneously oxidized or corroded. If brass be electrically connected to metallic iron and the two be placed in strong cupric chloride solution, the iron will be the anode and the brass the cathode. The action, however, is not merely a displacement of copper by iron, since the cathode is gradually corroded away, or converted into a mass of loose copper crystals. It is not possible to explain either of the foregoing examples of the corrosion of the cathode on the assumption that such corrosion is due to local couples formed on the surface of the cathode, since the potential of every point of the surface of the cathode is below that of the liquid, and consequently no metal can pass into solution electrochemically; moreover, the action can be obtained with highly purified copper substituted for the brass, the corrosive attack on which can be shown to be independent of the distribution of any impurity present."

This is the same fallacy, that a pure metal is incorrodible, plus the explicit assumption that local action is always chemical. If the corrosion of copper by nitric acid is chemical and not electrolytic, the case is proved and there is no need of going any further. If the corrosion of copper by nitric acid is electrolytic, it is still electrolytic even though we superpose another electrolytic action. This corrosion of the cathode used to be trotted out as an argument against the chemical theory of the voltaic cell[1] nearly a hundred years ago and it has rather lost its effectiveness as a bugbear. Fechner[2] set up a cell, $Zn/H_2O/Cu/acid/Zn$. Although the acid attacked the impure zinc of those days with violent evolution of hydrogen, the zinc in the water solution was the anode. Fechner considered this a conclusive experiment against the chemical theory of the voltaic cell and now we have a cell involving practically the same principle cited as a conclusive experiment against the electrolytic theory of corrosion.

Bengough and Stuart[3] state that "the fact that local action is quite independent of the existence on metallic surfaces of cathodes and anodes is shown by the fact that any selected portion of a metal can be caused to suffer heavy local corrosion if the conditions external to the metal are suitably controlled. A simple way of showing this is to tie a piece of ordinary string round a piece of copper or brass and immerse the whole in sea-water. Active local corrosion will take place beneath the string in spite of the fact that access of oxygen to the corroded area is apparently greatly lessened. Local corrosion at any selected spot can also be produced beneath cotton-wool, coke, glass fragments (if not in too fine a state of division), paraffin wax (whenever liquid can penetrate beneath the wax,) and many other bodies. No such action takes place, however, beneath a deposit of red lead, which is an excellent depolarizer. Any purely electrochemical explanation of these phenomena is ruled out by the

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[1] Ostwald: "Elektrochemie," 485 (1896).

[2] Schweigger's Jour. Chem. Physik, 57, 9 (1829).

[3] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 66, 90, 98 (1922).

fact that they can be brought about by such insulators as glass and paraffin wax."

The authors' explanation of this (p. 98) is very obscure. In the first paragraph they say that "the preceding theory indicates that the ordinary local corrosion essentially consists in direct oxidation of the metal by dissolved oxygen. The reaction may be simply oxidation of the massive metal; but possibly the metal surface is then disintegrated by the corroding liquid to form colloidal metal and then oxidized. The resulting colloid acquires a charge under conditions whereby the metal holds the equivalent opposite charge, and these charges are only neutralized in presence of electrolytes. The colloid is thereby precipitated by the anion, and the corresponding cation discharged on the metal surface."

I understand the first sentence of that paragraph and believe it to be wrong. I do not understand the last sentence but it sounds like reversed electrolysis and neither the authors nor I believe in that. While we have never done any work on this type of localized corrosion at Cornell, I am quite willing to accept the explanation offered by Evans (p. 118) that the oxygen-free portion is normally the anode and the oxygen-rich portion is normally the cathode.

Bengough and Stuart[1] have produced corrosion "without the use of any substance other than water and air." They let a jet of water or salt solution carrying entangled air bubbles impinge on the metal. They find that a strip of iron corrodes on the side away from the jet, which means that the oxygen-poor portion becomes anode and the oxygen-rich portion becomes the cathode. This is exactly what one would expect on the basis of the electrolytic theory of corrosion. If we are dealing with a gas cell, the oxygen must form the cathode. The only difficulty with this is that copper behaves in the opposite way, the side where the jet impinges becoming anodic and not cathodic as in the case of iron. It is not surprising that Bengough and Stuart should say that "clearly, it would be very difficult to form a general theory of corrosion on the lines of an oxygen concentration cell which took into account both these sets of facts," and yet it is a pity that they did not study the matter further.

When Bengough and Stuart showed me these experiments in London last year, I admitted, because I had to, that I had no explanation to offer for the phenomenon; but the electrolytic theory of corrosion is right when properly applied and consequently I made the prediction that they had overlooked something, though I did not know what it was. On my return to Ithaca we started some experiments, varying the conditions. We placed two similar electrodes in a beaker containing M/1 or M/2 sulphuric acid, short-circuited the cell on a Weston milli-ammeter, and bubbled air against one of the electrodes. We confirmed the results of Bengough and Stuart in every respect. The electrode, against which air is bubbled, becomes cathode in the case of nickel and iron and anode in the case of copper. The differences of potential,

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[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 66, 125 (1922).

as measured roughly with a milli-voltmeter, were of the same general order 0.5-2.0 millivolts.

Mr. Vieweg then had the brilliant idea of bubbling hydrogen against one electrode. Distinctly to my surprise, the results were qualitatively the same, the electrode, against which the gas bubbled, being cathode in the case of nickel and iron, and anode in the case of copper, the observed voltages being somewhat lower than in the case of air. Since the phenomenon appeared not to depend primarily on the nature of the gas, similar experiments were made with nitrogen and with illuminating gas with similar results.

A few quantitative corrosion experiments were then made using a solution of 28 cc. ethyl alcohol and 60 cc concentrated sulphuric acid diluted to one liter with water. The two short-circuited copper electrodes were separated by a porous cup and the gas was bubbled against one of them. With nitrogen, the electrode against which the gas was bubbled lost 48 mg while the unexposed electrode lost 5 mg in seventeen hours. With oxygen the exposed electrode lost 20 mg and the unexposed one 2 mg in three hours. With hydrogen the corresponding losses were 20 mg and 3 mg in nine hours. The corrosion is of the same order of magnitude in all three cases; but the actual rate of loss in oxygen is two to three times as much as in either of the other gases.

It is evident that we are dealing with frictional electrification, a phenomenon which has not hitherto been considered in corrosion research. It is worth noting that these results agree satisfactorily with Lenard's observations on the electrification of drops of water in different atmospheres. One wonders whether the method of preparing the standard hydrogen electrode really gives accurate values. It is of course possible that this effect may be negligible with platinized platinum; but the mere possibility of an error of the order of a millivolt is a bit startling. It is to be hoped that some of the people who specialize in accurate measurements will look into this.

Having eliminated the electrolytic theory of corrosion to their own satisfaction in many cases, Bengough and Stuart[1] state that "it remains to determine the nature of the reaction which does produce corrosion. The following considerations deal with the corrosion of single metals, and couples of which both metals corrode very much as when separated. Such couples in general show only small potential differences. It must be clearly understood that electrochemical action does predominate in the corrosion of other couples, the metals of which corrode in a manner different from that of the separated metals, and which show considerable differences of potential.

"Leaving aside the latter, it is clear that there is some factor present in local corrosion the effect of which has become much more important than difference of potential. This factor is undoubtedly the 'scale'. The term 'scale' has been defined as the mixture of solid, gelatinous, and colloidal substances which is formed by corrosive action and remains in the neighborhood of the metallic surface. Corrosion has already been defined as the oxidation of a metallic substance, using the term 'oxidation' in its general sense. Two

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[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals.' J. Inst. Metals, 28, 85 (1922).

well-defined types of corrosion, differing markedly in their effects on the metal surface, can now be distinguished from one another:

"(A) All corrosion products, except hydrogen and displaced gas or metals, completely soluble in the corroding liquid, giving true solutions. In such cases the metal surface is comparatively evenly attacked, and the solution-tension theory gives a reasonably correct account of the phenomena observed, though a strictly electro-chemical application of it is not necessary. Examples: sodium in water and zinc in hydrochloric acid.

"(B) One or more corrosion products comparatively insoluble in the corroding liquid and closely adherent to the metal surface. Metal surface usually attacked locally, giving isolated 'pits'.

"It is important to notice that to obtain well-defined corrosion of type B the product must adhere closely to the metal. Thus aluminum amalgam in distilled water shows the first type of attack (type A), since the aluminum hydroxide, though insoluble, does not adhere to the metal surface.

"With some metals, *e.g.* sodium, aqueous solutions always produce the first type of attack, since sodium hydroxide and sodium salts are readily soluble. Most of the metals in commercial use, however, can be made to undergo either type of corrosion by varying the nature of the corroding liquid. Thus zinc is fairly evenly attacked by dilute acids, even by very dilute acetic acid (type A), but in distilled water becomes deeply pitted and covered with gelatinous zinc hydroxide. In neither type of corrosion is there any definite evidence that the action at the metallic surface is electro-chemical in character."

"The points in connection with local corrosion have already been fully considered, and will now be briefly summarized:

"The corrosion of zinc in distilled water may be taken as an example of local corrosion (type B), and the following facts should be noted:

"1. No evolution of hydrogen can be observed, although considerable corrosion takes place. This is in sharp contrast to the behaviour of zinc in very dilute acid, where the evolution of hydrogen is quantitative.

"2. Pits rapidly develop, and the surface of the metal round each pit becomes covered with gelatinous adherent deposits of zinc hydroxide, which often protect the surrounding metal from corrosion for considerable periods.

"3. If the pits be examined under the microscope while the metal is still wet, they will appear to contain nothing but clear transparent liquid. The bright metallic surface at the bottom of the pit is clearly visible.

"The most obvious feature of such corrosion is that intense action takes place at a particular spot, producing a pit in the metal, while the surface immediately surrounding this pit remains comparatively unattacked. Superficially considered, this observation seems to support the electro-chemical view very strongly, the pit being regarded as an anode, and the surrounding metal as the corresponding cathode. But it has been noted that this view will not bear close investigation, since, for instance, no such local action occurs in dilute acids, although the action at the pit in distilled water may be more rapid than that occurring anywhere over the surface in acid."

We can agree heartily with Bengough and Stuart that the question of surface film or scale is all-important in the study of corrosion. After the smoke of battle has cleared, that will be the point on which we ought all to get together, to study the conditions affecting the formation and properties of surface films on metals. The work must be done definitely and specifically in each particular case and we must keep clear of the vague phrases which are painfully common at present.

While agreeing absolutely with Bengough and Stuart that the study of film formation is the vital thing in the problem of corrosion, it must be recognized that there is nothing strikingly new about this, though most of the research in the past has been along different lines. Cushman and Gardner[1] have a few pages on the protection of iron by the production of surface films of magnetic oxide or other substances. I have myself called attention to the bearing of surface films on corrosion[2] and this has been emphasized by Curry.[3] Walker[4] cited the case of aluminum and of copper-bearing steels. E. A. Richardson and H. K. Richardson[5] point out that "while it may be true that the initial rusting is largely electrolytic in character, other factors, such as the adherence of the rust and the protection thereby given to the metal, come into operation and outweigh any electrolytic corrosion—a conclusion that has also been arrived at by other observers. W. D. Richardson[6] has recognized three types of rust. My experience[7] at the same meeting was that people were only too glad to take up the detailed study of protective films and, in fact, it was as a result of that symposium[8] that the present Corrosion Committee of the National Research Council was formed and that this report was written.

While we know very little about the properties of surface films, there is one case which calls for special mention. Bengough and Stuart[9] point out that "as regards both copper and brass, the usual effect of cold-working the metal by punching, drawing, or rolling is to retard slightly the rate of corrosion both local and general, provided the finished surface is smooth, owing to the formation of a thin film of flowed material that is somewhat more resistant to water corrosion than the underlying crystalline material. . . . The protective effect of the flowed layer is best seen on smooth surfaces; on roughly cut surfaces and edges, such as are formed by a hacksaw, the layer is not sufficiently uniform and continuous for good protection of the underlying metal.[9] In acid the effect of flowed layers is not so conspicuous, and they probably depend for their effects, partly at any rate, on oxide films formed during the period of mobility."

It is a matter of general knowledge that highly polished surfaces show a surprising resistance to corrosion. Whether one considers the polished surface

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[1] "Corrosion and Preservation of Iron and Steel," 158 (1910).

[2] Bancroft: Trans. Am. Electrochem. Soc. 9, 17 (1906).

[3] J. Phys. Chem. **10**, 484 (1906).

[4] Trans. Am. Electrochem. Soc. **29**, 436 (1916).

[5] Trans. Am. Electrochem. Soc. **39**, 69 (1921).

[6] Bancroft: Trans. Am. Electrochem. Soc. **39**, 211; Fink: 259 (1921).

[7] Corse: Trans. Am. Electrochem. Soc. **39**, 258 (1921).

[8] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, **28**, 68 (1922).

[9] This matter has been more fully discussed in the Fourth and Fifth Reports.

to consist of very fine crystals or of an amorphous layer as Beilby does, it must be anode against a normal surface and should therefore corrode more readily if everything else were equal. In this case one must assume, as Bengough and Stuart[1] do in another case, that a more coherent film forms on a very smooth surface. "If perfectly *pure* metal be exposed to water, oxygen, and electrolyte, a continuous protective gel will probably be formed over the whole surface of the metal. No appreciable corrosion will take place as long as the gel does not change. This is doubtless the explanation of the fact that Lambert's pure iron remained apparently uncorroded, even when exposed to tap-water and ordinary air.[2] The greater "homogeneity of the iron" ensured a continuous protective film, and the inhibition of corrosion throws no light on the question of differences in solution pressure over the actual metal surface. Such iron would necessarily give no reaction under the ferroxyl test, as charged colloid is not being given off at any point on the metal. The presence of such an extremely thin gel film over the metal would be extremely difficult to detect. Thus freshly cut aluminum is supposed to become instantly covered with a film of oxide; but the metal remains perfectly bright. The corrosion of Lambert's pure iron in sodium chloride solutions would seem to be due to subsequent chemical or physical alteration of the gel film by the salt solution."

It is a pleasure to find myself in agreement with Bengough and Stuart in the opinion that Lambert's pure iron was covered with a film of some sort. Since an annealed metal becomes more crystalline and therefore probably rougher on the surface, this may account for the more rapid corrosion of the annealed metal in many cases. It is quite possible that some of the conflicting data in regard to the effect of strain may be due to differences in surface under the different conditions. Bengough and Stuart[3] consider that non-metallic impurities in the metal surface may prevent the formation of a film at those points and that such a perforated film may not prevent corrosion, which will develop at the pore. There is no doubt that these things may work this way and there is no doubt that a film with pin-holes in it will not give effective protection. The canners have had plenty of experience along those lines. On the other hand it is not safe to make the generalization that this will always happen. It has already been pointed out that cast iron shows an unexpected resistance to corrosion under certain conditions and nobody could have predicted the behavior of the copper-bearing steels or of certain of the copper-tin bronzes. It is true that the impurities in the last two cases are not sonims; but it will be much safer not to indulge in too many predictions along this line for the present.

There is no question but that the problem of the properties of the surface film is a problem in colloid chemistry. On the other hand we have not explained anything when we say colloids; we have merely indicated a line of

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[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 95, 107 (1922).

[2] Lambert: J. Chem. Soc. 101, 2068 (1912).

[3] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 95 (1922).

attack. This is a point which is often overlooked. There is no doubt, for instance, but that the plasticity of clay is due to colloids; but we have not explained anything by that. It is still necessary to show how and why the colloidal material acts, and we must show it in detail. One cannot accept the suggestion of Friend[1] that bichromates inhibit the corrosion of iron because they coagulate the ferric hydroxide sol since we know that they act by making iron passive and we know that the passivity of iron is not due to ferric oxide. In another paper Friend[2] gives a new theory of the corrosion of iron which seems to be that ordinary iron reacts with oxygen in presence of water to form a ferrous hydroxide hydrosol which is particularly reactive chemically, and which oxidizes, producing ferric hydroxide hydrosol "in the most favorable circumstances. This higher hydrosol is now alternately reduced in contact with the iron and oxidized again by atmospheric oxygen, thus catalytically accelerating the oxidation of the metal. When the sol flocculates or precipitates out, it yields rust."

So far as I can see, one could substitute the word copper for iron in this theory and prove that copper rusts in the same way as iron does. Also, the peroxide plate of the storage battery would be quite impossible to maintain, because the lead peroxide would react with the underlying metal to form lead oxide. I rejoice that Friend has emphasized the colloidal side of the problem but I cannot see that his papers indicate any real progress. I object very strongly to his calling it a new theory and to his saying that the electrolytic theory of corrosion is inadequate to account for the facts. All he really means is that we must consider the properties of the corrosion products and that these corrosion products are often colloidal; but we don't question that. If he had said what he really meant, it would have done some good; but, as it is, he has done actual harm, though not much, in an attempt to make his paper seem more of a step forward than it really is. Bad advertizing does not pay.

There is nothing to be gained by criticizing Bengough and Stuart's applications of colloidal chemistry. They are very weird and the best one can say for them is that they do call attention to the colloidal side of the problem. Bengough and Stuart[3] summarize their hypotheses as follows:

"A metal immersed in water sends positively charged metal ions into the liquid, and becomes itself negatively charged. In the case of ordinary commercial metals, the metal also becomes superficially oxidized if dissolved oxygen is present. The hydroxide produced by this oxidation can take up the ions given off by the metal, and the hydroxide thereby passes into the state of a positively charged colloid. Some of this colloid will diffuse away, permitting further reaction between the oxygen and the metal surface, and thereby re-forming the hydroxide film over the latter. Oxidation is then stopped till this hydroxide can pass into the colloidal state by acquiring positively charged metal ions. This, in general, does not take place till the colloid

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[1] J. Chem. Soc. 119, 937 (1921).

[2] Trans. Am. Electrochem. Soc. 39, 63 (1921).

[3] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 33 (1922).

initially formed has diffused into the presence of electrolyte, when it is precipitated by the anion of the dissolved salt, the cation neutralizing the charge on the metal corresponding to that on the colloid. This allows the metal to send more ions into solution, and the uncharged hydroxide thereby acquires a charge. If the colloid so produced can diffuse away, the process can continue and corrosion develop.

"For steady corrosion, therefore, the colloid must be produced under conditions which allow it to diffuse some distance from the metal before precipitation. If it precipitates directly on the corroding surface it will, in general, adhere to the latter and stop corrosion. In the case of a corrosion pit, the first condition is fulfilled, since no precipitation occurs inside the pit. It is only when the colloid diffuses through an aperture (generally very small), in the gel-deposits at the mouth of the pit, that it meets electrolyte and is then precipitated. Such precipitation merely thickens the external gel-deposits. These gel-deposits adhere directly to, and protect, the metal surrounding the pit, and thereby emphasize the local nature of the corrosion."

Bengough and Stuart[1] justify their contention of direct oxidation of the metals by the statements that "at temperatures at which no *liquid* water can be present, it is clear that such corrosion can and does take place, since no electrolyte is present; as an instance of this type of action the formation of temper colours on steel at, say 230°C, may be quoted, and this is clearly a molecular and not an ionic reaction. . . . Küster[2] has shown that liquid water is not necessary for the corrosion of sodium at the ordinary temperature, since water vapour will readily attack it." They might also have added that sodium burns in air to sodium peroxide, which it does not do in presence of water.[3]

I admit frankly that I do not know whether the oxidation of iron at 230° is or is not a molecular reaction. I know that it does not take place in perfectly dry air and that one can drop dry sodium into a flask containing boiling bromine without any reaction taking place, provided the bromine is dry. Until we know more about the theory of combustion than we do now, I am very reluctant to base conclusions on such premises until we are forced to.

I have purposely avoided any reference to non-aqueous solutions, though some instances have been cited triumphantly by Bengough and Stuart,[4] because I believe in attacking the relatively simple problem first. Of course, we must struggle with the non-aqueous solutions some day; but I do not see how to attack them profitably at present. So far as aqueous solutions are concerned, I believe now, as I have for years, that any special corrosion problem can be accounted for satisfactorily and quickly if the investigator makes use of the electrolytic theory of corrosion, the facts of chemistry, and common-

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[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 41, 52 (1922).

[2] Z. anorg. Chem. 41, 474 (1904).

[3] Dry oxidation is differentiated sharply from wet oxidation by Haber: Z. Elektrochem. 7, 445 (1900).

[4] "Sixth Report to the Corrosion Research Committee of the Institute of Metals." J. Inst. Metals, 28, 52 (1922).

sense. These problems are not mysterious in any way; it is we who make them seem so.

Since the first draft of this report was written, there has appeared an article[1] on "The Electrochemical Character of Corrosion" by Evans which also controverts many of the points raised by Bengough and Stuart. "It seems likely, indeed, that the oxidation of metals in air at high temperatures, which appears to proceed in the absence of any moisture, must be regarded as a direct chemical attack. On the other hand, at ordinary temperatures the observed phenomena of corrosion, as far as they are known at present, correspond closely to those which could be predicted from fundamental electrochemical principles. Consequently here theories of 'pure chemical corrosion' are at present superfluous, although it is possible that real cases of 'pure chemical corrosion' at low temperatures may be discovered by future research. Those who at present assert that the ordinary corrosion of common metals, like zinc and lead, are cases of simple chemical oxidation, may be asked why the electrochemical corrosion which would be predicted from our accurate knowledge of electrode potentials fails to occur. Only when they have explained the absence of electrochemical corrosion are they entitled to construct theories regarding chemical corrosion."

Evans[2] is rather sympathetic with Lambert's point of view. "We are now in a position to approach the subject of electrochemical corrosion. Let us consider a piece of metal immersed in a liquid. If the metal is absolutely uniform, both chemically and physically, the potential between metal and liquid will be the same at all points, and no current can be set up. No electrochemical corrosion is therefore to be expected. It is significant here to recall that, in the case of iron and lead, Lambert and his coworkers[3] have actually succeeded in preparing materials so pure and uniform that they do not corrode under conditions which allow rapid attack of materials of merely 'ordinary purity.'

"If, on the other hand, the metal is not uniform, varying from place to place either in chemical or physical character, it is certain that at the moment of immersion there cannot be equilibrium. The potential will vary from point to point, and a current (momentarily at least) must be set up between the different points. At certain places (the anodic areas) the metal will commence to pass into the ionic condition; at other places (the cathodic areas) hydrogen ions will be discharged (assuming no other metallic ions are present in solution), and elementary hydrogen will commence to alter the potential of the cathodic areas in a negative sense, thus making it more nearly equal to the potential at the anodic areas. If this process of hydrogen accumulation continues until the potentials at the originally anodic and cathodic areas become equal, equilibrium will be established, and in such a case there can be no appreciable electrochemical corrosion.

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[1] J. Inst. Metals, 30, 239 (1923).

[2] J. Inst. Metals, 30, 244 (1923).

[3] Lambert, Thomson, and Cullis: J. Chem. Soc. 97, 2426 (1910); 101, 2056 (1912); 107, 218 (1915).

"Two occurrences, however, may prevent the establishment of equilibrium. Before the potential at the cathodic areas becomes equal to that of the anodic areas, the cathodic areas may become so supersaturated with hydrogen that the gas begins to stream off in bubbles, in this case, corrosion of the metal at the anodic portions will continue indefinitely, the rate being equivalent to the rate of production of gaseous hydrogen at the cathodes; we may call this the Hydrogen-Evolution Type of Corrosion. If, however, the conditions are not such as to allow the evolution of gaseous hydrogen in bubbles, a relatively slow removal of hydrogen from the cathodic areas may take place if oxygen (or an oxidizing agent) is present in the solution; this will allow the corrosion of the metal at the anodic areas to continue, but the rate will be limited by the rate of diffusion of dissolved oxygen (or the oxidizing agent) across the layer of liquid next to the metal; we may term this kind of corrosion the Oxygen-Diffusion Type."

Evans points out that "magnesium, for instance, scarcely reacts with pure water; but the presence of a soluble chloride in the water causes the formation of the hydroxide in a 'loose form', and has thus an 'activating' effect on the metal, and allows a vigorous evolution of hydrogen." In another passage he points out that this loosening effect is probably akin to peptization.

"If now we consider the reaction of a metal in a solution without contact with platinum-black, we have to take considerations of over-potential into account. The condition needed for the evolution of hydrogen in bubbles will become

$$\pi_H - \phi - \pi_M > 0,$$

where ϕ is the overpotential of the cathodic areas. Thus metals like tin, lead, and nickel, which stand close to hydrogen in the potential series, at ordinary temperatures do not readily displace hydrogen in bubbles from dilute acids; they may do so, however, if the solution is warmed, so as to diminish the overpotential. Even zinc does not displace hydrogen readily from acids when pure, in spite of its position near the "reactive" end of the potential series; but if it contains noble impurities of low overpotential value, the gas is evolved more rapidly. Commercial zinc evolves hydrogen slowly at first, but after " a period of induction" the reaction becomes quite vigorous, owing to the accumulation of a black deposit of the noble impurities on the metallic surface."

"If the conditions are such that hydrogen cannot be evolved as a gas, it may yet be removed from the cathodic areas slowly if dissolved oxygen is present in the solution at these points. This is found to be the case; metals like iron, nickel, cadmium, and lead, which do not displace hydrogen in bubble form when placed in a neutral solution, nevertheless are corroded slowly by a neutral solution (say, a solution of sodium chloride) containing oxygen; likewise copper, which cannot cause the evolution of hydrogen gas from dilute acids, dissolves slowly in these acids in the presence of oxygen.

"This type of corrosion will always be slow; for rough purposes, we may say that a maximum rate is fixed by the rate of diffusion of oxygen across the layer next to the metallic surface. Consequently, within certain limits, the rate of corrosion will be nearly independent of the conductivity of the solution. There is no reason why oxygen should diffuse more quickly through a highly conducting liquid than through a badly conducting liquid. If anything, oxygen will actually diffuse less quickly through a solution of a salt than through pure water, because the presence of a salt generally depresses the solubility of oxygen in water."

"The electrochemical prediction of corrosion would lead us to regard as possible the attack of metal at points to which dissolved oxygen has no direct access. The presence of oxygen is only needed at the cathodic areas; at the anodic areas its presence will, if anything, be unfavourable to the reaction. It is interesting to find that specially marked corrosion often occurs at points to which oxygen can only diffuse very slowly—for instance, at the bottom of pits or over areas covered with porous substances, such as string or fabric.

"The electrochemical corrosion of a metal by, say, sodium chloride, should produce the metallic chloride at the anodic portions, whilst the discharge of hydrogen ions on the cathodic portions will leave the liquid alkaline at these points; where the alkali and the metallic chloride diffuse together, the metallic hydroxide will generally be precipitated, often as a membranous web or a gelatinous precipitate; this phenomenon has been observed in practice.

"If, however, the metal is immersed in a solution containing an anion which forms an insoluble salt with the metal in question, the primary product at the anodic areas will be an insoluble substance; under certain circumstances this may adhere to the anodic areas and protect or ennoble them, thus causing corrosion to cease. Numerous examples of this effect are known; perhaps the most important case is that of lead immersed in waters rich in carbonate.

"The formation of a protective film, is, however, not confined to cases of this kind. It is well known that when an external e.m.f. is applied to an electrolytic cell fitted with an iron anode immersed, say, in a sodium sulphate solution, a low current density will give rise to the formation of soluble iron sulphate. But there is always the possibility that instead of the discharge of SO_4'' ions, the discharge of OH' ions may occur. If the current density is raised unduly, something in the nature of an invisible oxide film (possibly a layer of adsorbed oxygen atoms) is produced, and the iron becomes "passive"; the layer retards the anodic dissolution of the iron, whilst permitting the production of oxygen gas; I have discussed this subject elsewhere.[1] With an aluminium anode the effect is even more striking; a porous oxide film containing oxygen gas in the pores is produced, and this prevents the passage of current altogether in one direction; in other words, aluminium refuses to function as an anode, unless certain substances (notably chlorides) are present, which cause the film to break down."

Evans[2] makes the same mistake that Bengough and Stuart did in postulating that potassium bichromate and potassium chromate are powerful oxidizing agents. The discussion of the oxidation of apparently dry metals is apparently sound and certainly interesting. "It has been stated that in

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[1] U. R. Evans: Trans. Faraday Soc., 18, 1 (1922).
[2] J. Inst. Metals., 30, 251 (1923).

general the conductivity of the liquid should be only a minor factor in determining the rate of corrosion. In one case, however, the conductivity becomes of great importance. This is in the corrosion of "apparently dry" metals by air. If a metal is truly dry, it does not corrode in dry air at low temperatures, but if an invisible film of adherent water is present, corrosion may occur. The thinness of the film will restrict the current flowing between anodic and cathodic areas, and if the film is composed of pure water the attack must be extremely slow. If, however, the atmosphere contains volatile electrolytes, such as hydrogen chloride or sulphur dioxide, these may be expected to dissolve in the water and increase the conductivity of the film, and thus accelerate the corrosion; if, further, the corrosion product has a hygroscopic character, it may be expected to absorb further water from the atmosphere, and by increasing the thickness of the film, increase still more the rate of attack. I have shown experimentally that both these expectations are realized.

"The work of Pilling and Bedworth[2] has shown that at high temperatures the direct oxidation of metals by air, even in the absence of water, is possible; but, as the oxide film grows thicker, the rate of diffusion of oxygen through it becomes slower, until finally a thickness is reached at which further oxidation becomes negligibly slow. The thickness attained will of course depend on the temperature. On iron the oxide film produced at 290°C. is capable of extinguishing (by interference) the yellow rays of light, causing a blue "temper colour"; at 230° the film is thinner and the blue rays are extinguished, the temper colour being therefore yellow; below 200°C. the film is too thin to cause the extinction of any visible rays, and clearly at ordinary temperatures the thickness of the film caused by direct oxidation will be negligible. It is evident, therefore, why the presence of a moisture film and an electrolyte is needed for rapid corrosion at ordinary temperature; the hydroxide or oxide formed by interaction between the soluble salts from the anodic areas and the alkli from the cathodic areas will not necessarily form a protective coating over the whole surface, and will therefore not necessarily bring the action to a standstill."

On p. 254 Evans says that "the type of corrosion where hydrogen is liberated in bubbles is already generally admitted to be electrochemical in character. Consequently only a few experiments were conducted on this type, to investigate certain points which seemed in doubt. . . . Cadmium was found to be practically unaffected by normal hydrochloric acid in the absence of other metals, no doubt owing to its high overpotential value. Contact with nickel —or even with iron—caused the evolution of hydrogen from the second metal. Contact with copper caused only a slow evolution of hydrogen from the copper; whilst contact with lead—a metal of high overpotential—had no effect." This is interesting, because apparently an alloy of cadmium and lead would not corrode readily in spite of the surface being heterogeneous.

"The type of corrosion wherein no hydrogen is liberated in bubbles is considered by some authors, notably by Bengough and his co-workers,[3]

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[1] U. R. Evans: Trans. Faraday Soc., 19 (1923).

[2] N. B. Pilling and R. E. Bedworth; J. Inst. Metals, 29, 529 (1923).

[3] J. Inst. Metals, 21, 37 (1919); 28, 31 (1922).

to be due to the direct chemical oxidation of the metal by oxygen, and not to electrochemical action. Consequently, extensive experiments were performed, with a view to ascertaining whether the action was electrochemical or not. . . .

"Bengough and Hudson,[1] in 1919, found that when cast zinc was suspended in "distilled water" certain white vertical striations, formed of zinc hydroxide, were produced upon the surface. I obtained rather similar results with cast zinc, and also obtained well-marked striae upon sheets of *rolled* zinc placed in a vertical or nearly vertical position in glass tumblers half-filled with liquid. The plate could be obtained with zinc of variety "A", but is better developed on the less pure varieties of zinc. It could be produced best in a N/2 potassium chloride solution; but a somewhat similar phenomenon was obtained in ordinary laboratory distilled water, or even in "conductivity water" having a conductivity of 2×10^{-6} mho-cms. (*i.e.* the same quality of water as that used by Bengough and Hudson; it is, of course, far from being "pure water", which has a conductivity of about 4×10^{-8} mho-cms,). The striations appear within a few hours of the immersion of the metal and continue to develop during several days. The general appearance of the striae in the early stages of corrosion often recalls the tracks made by rain-drops running down a window-pane, and suggests that they are formed by drops of some heavy liquid sinking down along the surface of the zinc; the tracks are bounded on each side by a thin membranous wall of zinc hydroxide. There is a more or less continuous barrier of zinc hydroxide separating a nearly uncorroded area near the water-line from the corroded portion below; in places this wall may stand out for a distance of 1 to 2 mm. from the surface of the zinc. Where potassium chloride solution is used there is a great deal of flocculent zinc hydroxide at the bottom of the tumbler, in addition to that attached to the metallic surface; it is evident that the attack upon the zinc is very much more pronounced when potassium chloride is present than when "distilled water" is used—a fact which has been confirmed by experiments with weighed specimens.

"If after the formation of these striae the metal is removed from the liquid, allowed to drain, and is then tested with phenolphthalein, it is found that alkali is present. The walls of zinc hydroxide become pink;[1] but where potassium chloride solution has been used, a much greater amount of alkali is present on the uncorroded portion close to the water-line; very little alkali seems to be formed below the main hydroxide "barrier."

"The electrochemical view of corrosion suggests a very simple explanation of these phenomena. The oxygen-rich portions near the water-line become cathodic, and the test of the zinc, where the supply of oxygen cannot be renewed, becomes anodic. Alkali is produced at the cathodic portions, and

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[1] The production of the pink colour where "distilled water" has been used to develop the striations may be explained either by the supposition that pure zinc hydroxide is alkaline, or by the presence of minute quantities of sodium or potassium salts in the distilled water. Preliminary experiments with water condensed in quartz show that the pink colour is still produced with this water, but it is possible that small amounts of sodium salts were introduced with the zinc or from the emery-cloth. It is hoped to carry out further work on this subject.

diffuses outwards into the body of the liquid; zinc chloride (or some other zinc salt) is produced at the anodic points lower down, but being heavy it tends to sink down along the metallic surface. The membranous walls of hydroxide simply represent the surfaces where the alkali and zinc salt have come into contact and have reacted together."

"Bengough and Hudson[1] found, in 1919, that if two pieces of copper placed in a divided cell were joined to the poles of a galvanometer, and if air was bubbled over one piece, that piece became *anodic*; thus copper shows a behaviour which at first sight is the exact converse of that displayed by zinc, cadmium, iron, and lead.

"It seemed most important to investigate this anomaly, and, after numerous experiments, it became clear that the potential of copper immersed in potassium chloride solution was affected to an important extent by three types of treatment:

(a) *Aeration.*—The presence of oxygen tends to render the potential more *positive*, as in the case of all other metals.

(b) *Stirring.*—The removal of an accumulation of copper ions from the metallic surface alters the potential in the *negative* direction, in accordance with the principle explained in Part I. of this paper.

(c) *Abrasion.*—The renewal of the surface by energy or scraping removes any protective film of cuprous chloride (or hydroxide) that may exist on it, and thus renders the metal "active," and shifts the potential in the *negative* direction.

"It was not easy at first to separate these three effects. They can best be demonstrated by using an *alkaline* solution made by adding 10 c.c. of normal sodium carbonate to 90 c.c. of N/2 potassium chloride. I have, however, satisfied myself that they also occur in a N/2 solution of potassium chloride to which no alkali has been added. If two copper electrodes are joined to a galvanometer and are immersed in the alkaline solution for some minutes, and one electrode is then taken out, dried, ground with emery and replaced, a current is produced, the treated electrode being the negative pole. The current produced in this way is comparatively large, but very fugitive; over 2 milliamps. were obtained momentarily between electrodes of immersed area 4×4 cm. If, on the other hand, two electrodes composed of the same type of copper, and having a similar electrochemical history, are immersed in N/2 potassium chloride until any current produced on first immersion dies away (this may sometimes require fifteen to thirty minutes), so that both electrodes are known to be covered with a film to the same extent, and if in this state the electrodes are alternately taken out into the air and replaced, a very much smaller current (usually only a few micro-amperes) is produced, the aerated electrode being always positive. The effect of stirring is seen if the electrodes are immersed in N/2 potassium chloride in a divided cell, one electrode being stationary, whilst the other is moved about; the electrode in motion becomes the negative pole. If both electrodes are stationary, but air is bubbled into one compartment, it is evident that both aeration and stirring will be pro-

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[1] G. D. Bengough and O. F. Hudson: Jour. Inst. Metals, 21, 122 (1919).

duced. It is found, however, that the effect of stirring greatly predominates over the effect of aeration, and that the current produced flows in such a direction as to make the copper over which bubbles are passing the negative pole. Since Bengough and Hudson used a stream of bubbles to "aerate" their copper, it is clear why they obtained a current passing in what at first sight may be regarded as the "wrong direction."

"If instead of using potassium chloride solution we use normal sulphuric acid, the abrasion effect ceases to be important, for obvious reasons; but the stirring effect becomes very pronounced and tends to mask the aeration effect. The effect of aeration can, however, be demonstrated by the following way. Two copper electrodes joined to a galvanometer are immersed in normal sulphuric acid. One is taken out, wiped dry with filter-paper, so as to expose the metal directly to the air, and replaced; a momentary current, sometimes reaching 3 milliamps. for electrodes of the dimensions given above, is produced, the aerated electrode being positive.

"It seems clear, therefore, that copper behaves towards aeration exactly in the same way as other metals, but that the effect may be masked by the effects of stirring and of abrasion. The effect of abrasion has been noticed in the case of other metals which are liable to become covered with "protective films", and needs no further discussion; but the influence of stirring requires special consideration at this point. Evidently the stirring removed the accumulation of copper ions from the neighbourhood of the electrode; such a removal will clearly shift the potential in a negative direction. It may be asked why the power of stirring to shift the potential in the negative direction is not noticeable in the case of zinc, cadmium, iron, and lead; in these metals stirring—in so far as it has any effect—tends to move the potential in the positive direction, by renewing the supply of dissolved oxygen at the electrode surface. A little consideration will show, however, that the effect of any accumulation of ions which is likely to be realized in practice will be negligible in the case of the more reactive metals, but will be very pronounced in the case of the noble metals; for at any given potential, the ionic concentration needed to put a stop to the passage into the ionic state is very high in the case of reactive metals, but very low in the case of noble metals."

The chief difficulty with this explanation is that, as has been mentioned, nitrogen and hydrogen act like oxygen. It is therefore a gas effect and not a question of oxidation at all.

"It seemed important to ascertain whether the general laws regarding the effect of aeration on the potential apply also to aluminum. It has often been asserted by critics of the electrochemical view of corrosion that the stable behaviour of aluminum towards corrosive agencies was in sharp contrast with the highly negative potential (-1.337 volt) usually assigned to the metal. One has to remember, however, that the experimental determination of the potential of aluminium is carried out with amalgamated aluminium—a material which oxidizes with great rapidity in damp air, and which has none of the stability associated with ordinary aluminium. Ordinary aluminium is clearly unsuited for the determination of the reversible potential, because it cannot function freely as an anode; such measurements of potential as have been made with ordinary aluminium give it a value very different from that attributed to aluminium in Table I.[1] If studied in the light of the extensive work of Schulze[1] on the valve action of aluminium produced by an *externally* applied e.m.f., the behaviour of aluminium immersed in different liquids—the knowledge of which we owe mainly to the work of Seligman and Williams[2]—becomes quite intelligible, and the facts seem to indicate that here also we are dealing with a case of valve action, but produced by an *internally* generated electromotive force.

"The rapid formation of a protective film on aluminium renders its study somewhat difficult. I found, however, that if two pieces of rolled aluminium were ground with emery, and were at once placed in a divided cell containing N/2 potassium chloride solution and joined to a microammeter, they show the aeration effect just as easily as any other metal. The withdrawal and replacement of either electrode produces a current, the aerated pole being always positive. After a few minutes, however, the current produced in either direction by aeration begins to be much smaller, although the effect of aeration can still be detected after five minutes. It is evident that the formation of obstructive films is responsible for the falling off in the sensitiveness, for if one electrode is treated afresh with emery-paper, it always becomes strongly negative (anodic) towards the other; boring or cutting of an electrode—processes which likewise expose a fresh, unoxidized surface—produce the same effect, the electrode so treated becoming negative. The conclusion may be drawn, therefore, that aluminium behaves towards aeration just in the same way as other metals, but the effect is complicated and often hidden by the formation of an obstructive skin.

"This matter is of some importance, since it serves to afford an explanation of certain phenomena observed by Seligman and Williams.[3] These authors came to the conclusion that the blistering of aluminium in hard industrial waters was connected with the presence of small cavities in the metal. They succeeded in reproducing the effect experimentally by making a number of small depressions in the metal and closing them up by hammering; on immersion typical "pits" and "blisters" were formed. Presumably the interior of the cavities to which oxygen could not diffuse readily became anodic, and consequently serious attack took place within the cavities. A similar explanation can be extended to the specially marked corrosion occurring over areas covered up by porous materials—a fact also established by Seligman and Williams.

"In my own experiments, it was found that if holes were bored in an aluminium surface, and the metal was then immersed in N/2 potassium chloride, a considerable amount of aluminium hydroxide usually formed over the mouth of the holes. But I am inclined to think that this was due to the

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[1] See, for instance, T. Heyrovský: J. Chem. Soc. 107, 27 (1920).

[1] Schulze: Ann. Physik, 21, 929 (1906); 22, 543 (1907); 26, 372 (1908).

[2] R. Seligman and P. Williams: J. Soc. Chem. Ind., 35, 88, 665 (1916): 37, 159 T (1918); J. Inst. Metals, 23, 159 (1920).

[3] R. Seligman and P. Williams: J. Inst. Metals, 23, 166-168 (1920).

presence of bubbles of air within the holes. . . . Thus, the phenomenon produced artificially by me is probably the exact converse of that which causes blistering in aluminium articles containing natural holes.

"Certainly, wherever air bubbles could be seen clinging to the aluminium surface, much flocculent aluminium hydroxide was produced in the liquid around these points. This was observed not only with the aluminium sheet, but also with utensils made of aluminium. Some aluminium teaspoons were immersed in N/2 potassium chloride solution, and air was bubbled through the solution for a few minutes; the spoons were then allowed to stand in the solution for two days. The greater part of the surface became tarnished and covered with a brownish-white deposit; but around and below the adherent air bubbles it remained comparatively bright, and at these places loose white aluminium hydroxide appeared in the liquid, as though produced by interaction between the alkali (from the cathodic areas around the bubbles) and the aluminium chloride (from the anodic areas elsewhere)."

Evans[1] draws a number of conclusions regarding the mechanism of corrosion. "If the experiments described above, dealing with eight different metals, are considered as a whole, it may be claimed that each part of the electrochemical mechanism of corrosion has been demonstrated. Where the metal is immersed in a neutral salt solution, it has been possible to show:

1. The production of a current.
2. The production of a metallic salt at the anodic portions.
3. The production of alkali at the cathodic protions.
4. The precipitation of hydroxide where they meet.

"If the aeration is uniform, it is apparently the distribution of impurities that determines which portions shall act as cathodes and which as anodes. If, however, the aeration is not uniform, then—provided there is a sufficient amount of noble impurities distributed throughout the metal as a separate phase—the cathodic and anodic areas are determined by considerations of the supply of oxygen, the "aerated" areas being cathodic and the unaerated anodic. Experiments on pure cadmium and lead seem to show that some impurities are actually needed on the aerated portions to act as cathodic particles; mere selective aeration of one area will not cause it to become cathodic, unless a suitable noble impurity is present. If, however, there are noble impurities scattered throughout all parts of the metal, the mechanism of selective aeration must be as follows. When one part of a piece of metal is aerated, and one is protected from aeration, the foreign particles in the protected area cannot (after the first moments) function as cathodes, because there is no supply of oxygen for the cathodic reaction. The foreign particles on the aerated portion act as cathodes, therefore, to the dominant metal in both areas; but in the aerated area the accumulation of insoluble corrosion product soon begins to interfere with the anodic function of the metal surrounding the foreign particles; and accordingly we are left with the foreign particles in the aerated area acting as cathodes, and the bright unobstructed metal of the unaerated area acting as anode. The anodic attack would be

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[1] J. Inst. Metals, 30, 278 (1923).

expected to be most pronounced in the portions of the unaerated area closest to the aerated area, as has been found to be the case.

"We thus obtain a rational explanation of the dangerous corrosion occurring at the bottom of pits and crannies, and other inaccessible places, as well as in areas covered with porous debris—a phenomenon well known to practical men. At such places, which are wholly anodic, owing to the absence of oxygen, the product of corrosion is generally a soluble metallic salt, which does not interfere with the subsequent course of corrosion. Over the accessible parts of the surface of a metallic article we may indeed temporarily experience electrochemical corrosion; but here the cathodic and anodic areas are close together, and insoluble metallic hydroxide is produced close against the metallic surface, and tends to protect it, and thus stop the action. The electrochemical explanation of the intense corrosion occurring at sheltered places is the only satisfactory one. Those theories, which attempt to account for the special corrosion at inaccessible points by assuming that flocculating electrolytes cannot reach these points (or that hydrogen peroxide is retained at these points and aids subsequent corrosion), involve many difficulties. If, for instance, diffusion through the mouth of a pit is assumed to be so slow that electrolytes cannot diffuse inwards (or that hydrogen peroxide cannot diffuse outwards), how can we account for the constant replenishment of oxygen within the pit? The electrochemical view of corrosion, which does not demand the presence of oxygen in the pit, is free from these difficulties.

"The production of a protective film on the anodic areas of the metal often introduces a complicating factor; this is most serious in the case of aluminium, but it was noticed in experiments on other metals that the current produced sometimes tended to drop off with the time. Indeed, the "influence of the corrosion product" is probably the most vital factor in determining the course of the later stages of corrosion. In the series of experiments described above, this complicating factor has been eliminated as far as possible by starting with specimens having a freshly ground surface. I have discussed the factors governing the question of the adhesion of the corrosion product elsewhere;[1] small changes in the composition of either the metallic phase or of the liquid may completely alter the degree of adhesion. The formation of a compact, protective film over the anodic portions of the metal will tend to "ennoble" the latter and to reduce the attack. On the other hand, the presence of a porous, gelatinous precipitate over these areas may act as a diaphragm, allowing the current to pass, but hindering the diffusion of oxygen to those areas; this will actually favour the reaction. In cases where a hydroxide precipitate is produced at the junction of the anodic and cathodic areas, it will presumably depend largely on chance convection currents in the liquid as to whether the hydroxide tends to move on to the anodic or cathodic area; in the former case, it may favour corrosion; in the latter case, by hindering the diffusion of oxygen to the cathodic area, it will tend to interfere with it."

Evans also says that "it has been proved that the unequal aeration of a metallic surface tends to produce intense corrosion at certain points, namely,

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[1] U. R. Evans: Trans. Faraday Soc., 38, 1 (1922).

those parts of the unaerated area which are most close to the aerated area. An important question, however, remains to be decided. Is differential aeration actually a necessary factor for corrosion, or does it merely cause the corrosion which would otherwise be distributed over the whole area to be concentrated at certain points? Experiments were conducted to settle this matter. . . . Apparently, the effect of restricting the access of oxygen to one part is not to increase the total corrosion of the specimen (at least during the early stages of the corrosion), but to concentrate on the unaerated area the corrosion which would otherwise be spread over the whole surface. Therein lies the danger of unequal aeration. An amount of corrosion which would be quite harmless if spread evenly over the surface of an article may become serious if confined to one particular area, whilst if it is concentrated within one single pit it may quickly cause perforation of the article in question."

Wilson[1] has made a careful study of the mechanism of the corrosion of iron and steel. "Regardless of the school of corrosion theory to which we may give our personal allegiance, there can be no real doubt but that the fundamental reaction in the corrosion of iron is essentially, as first pointed out by Whitney,[2]

$$Fe + 2\,H^{+} \longrightarrow Fe^{++} + 2\,H. \qquad (1)$$

As first stated by Walker,[3] the resulting hydrogen takes the form of a polarizing film which must be disposed of in some way before the reaction can long continue. This elimination of hydrogen may be brought about by either of the two following reactions:

$$2\,H + 1/2\,O_2 \longrightarrow H_2O \qquad (2)$$

$$2\,H \longrightarrow H_2\ (gas). \qquad (3)$$

"As between these reactions, investigations in this laboratory and in that of the National Tube Company have indicated beyond serious question that the amount of hydrogen evolved as such by the corrosion of steel in natural waters below 200°F is practically inappreciable compared with the oxygen consumed—except in the case of waters which are substantially oxygen-free, where the rate of corrosion is almost negligible.[4] It is evident, then, that, under these conditions, the amount of hydrogen removed by the third reaction is practically negligible, and that the rates of Reactions 1 and 2 in series almost always determines the rate of corrosion in natural waters. In neutral or alkaline solutions there is still another reaction—the oxidation of $Fe(OH)_2$ to $Fe\ (OH)_3$—which should be mentioned, but it practically never exerts an important influence on the rate of corrosion, though it does affect the character of the deposit formed." It would have been better if Wilson had laid more stress on the formation of an anode film such as one gets with sodium bichromate, even though this salt does not occur in natural waters.

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[1] Ind. Eng. Chem. 15, 127 (1923).

[2] J. Am. Chem. Soc. 25, 394 (1903).

[3] Trans. Am. Electrochem. Soc. 14, 175 (1908).

[4] This condition accounts for the appearance of small amounts of H_2 in closed-system hot-water radiators, where the oxygen is inappreciable and the rate of corrosion extremely low. In the case of steam heating systems the concentration of CO_2 in the condensed liquid tends to accelerate this action, owing to the higher hydrogen-ion content.

Wilson considers that with changing pH we get three fields. When the pH exceeds 10 or so, the alkalinity exerts an appreciable retarding effect on the rate of corrosion. When the pH falls below about 5, we get evolution of hydrogen. Between these two limits there is a stretch where the rate of corrosion is determined by the oxygen corrosion and is practically independent of the pH.

"Disregarding the electrochemical or any other theory of corrosion, and considering only the ordinary laws governing reaction rates it is obvious that in such a case where two reactions take place in series, whichever is inherently slower will determine the rate of both—except for a narrow intermediate range where the rates are nearly equal and a variation in either will affect the results. It is an experimentally observed fact, as shown by Walker[1] and others, that the rate of corrosion is directly proportional to the oxygen content of natural waters. It is therefore evident that the second reaction is controlling, and it must logically be concluded that the first reaction keeps enough hydrogen on the surface of the metal to care for the available oxygen, *regardless of the hydrogen-ion concentration* within the ordinary limits in natural waters.

"While this conclusion that the hydrogen-ion concentration should not appreciably affect the results in this range is surprising, it has been verified by recent experimental work. For example, the National Tube Company made experiments on the addition of varying amounts of caustic soda to Pittsburgh water, and found that increasing the calculated alkalinity from 0 to 100 p. p. m. did not appreciably affect the rate of corrosion in hot-water pipes. Similarly, experiments in this laboratory showed that treating a water originally slightly acid to phenolphthalein with enough alkali to give a titration corresponding to 30 p. p. m. NaOH did not affect the rate of corrosion at 70°F."

"As indicated previously, the flat central portion of the curves fortunately appears to cover most of the ordinary range of corrosion in natural waters, although the precise limits of this region are undoubtedly affected by a variety of conditions. It is comparatively simple to determine whether or not a given case lies in this region—if it is feared that the water may be so acid as to pass the right-hand limit, a determination of hydrogen evolved as gas or dissolved in the water would settle the question, whereas, if the question arises as to whether the alkaline limit has been passed, it is merely necessary to determine whether or not a slight decrease in alkalinity affects the results appreciably.

"Since it has been demonstrated that Reaction 2 determines the rate of corrosion in most natural waters, the question next arises as to whether the slowest phase in this reaction is the rate at which oxygen *diffuses in* to the metal surface, or the rate at which it *reacts* with the nascent hydrogen after reaching this surface. Either explanation could account for the rate being proportional to the dissolved oxygen content, but it should be readily possible to determine which is correct by noting the effect of stirring or the velocity of flow on the rate of corrosion—if the rate of reaction is the determining thing,

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[1] Walker, Cederholm, and Bent: J. Am. Chem. Soc. 29, 1251 (1907).

velocity should have little effect; whereas if diffusion determines the rate, velocity should have a pronounced effect. The following paper by Speller and Kendall[1] shows clearly that velocity has a very large effect, and it therefore indicates that the determining factor in the rate of corrosion is the rate of diffusion of oxygen through a stationary film of water adjacent to the surface of the metal. This is further borne out by the fact that if the rate of corrosion is calculated on the assumption that the oxygen must diffuse through a stationary film about 0.3 mm thick (the average of results calculated for the thickness of diffusion films at electrodes),[2] using approximate values from the literature for the diffusion coefficient of dissolved oxygen, the calculated rates of diffusion check well with the rates of corrosion observed by Speller and Kendall at moderate velocities and temperatures.

"The data of Speller and Kendall also confirm this conclusion in another way. Their results indicate that the rate of corrosion in pipes is very low and increases but slowly at low velocities, where straightline flow is known to prevail and then rises sharply in the critical region, and continues to increase, though less rapidly, as the velocity increases through the turbulent flow region. This behaviour is very similar to that observed by McAdams and Frost[3] for the coefficient of heat transfer from pipes to liquids, which similarly depend on the thickness of the stationary film on the pipe surface, through which heat must be conducted.

"This point being established, it is a simple matter to predict what factors should have a large effect on the rate of corrosion in natural waters, and what factors should be negligible under ordinary conditions.

"Since the rate of diffusion of oxygen through a stationary film is the determining factor in the wide intermediate range of hydrogen-ion concentrations, the variables which should have the largest effect on the rate of corrosion in this range are the oxygen content of the water and the velocity of flow past the steel surface. This checks precisely with the observations of Walker and Speller, respectively. The thickness and impermeability of rust films or other coatings would probably have a marked retarding effect. It is also conceivable that colloidal ferric hydroxide might have some catalytic action, as recently suggested by Friend.[4] Friend believes that colloidal particles of ferric hydroxide diffuse in and oxidize the iron and then diffuse out and take up oxygen from the water. The direct reaction between colloidal particles and the metal appears improbable in view of the overwhelming evidence that the latter is covered with the polarizing film of hydrogen, but Friend's results could just as readily be explained on the more reasonable assumption that colloidal ferric hydroxide is able to oxidize the nascent hydrogen film, and if it is present in large amounts as in beaker tests where the water is not

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[1] Ind. Eng. Chem. 15, 134 (1923)

[2] Wilson and Youtz: "The Importance of Diffusion in Organic Electrochemistry": Ind. Eng. Chem. 15, 603 (1923).

[3] J. Ind. Eng. Chem. 14, 1101 (1922).

[4] Trans. Am. Electrochem. Soc. 40, 63 (1921). This laboratory has not been able to check the surprising results of Friend which indicated a drop in corrosion at high velocities in natural waters, or a rise uniform with velocity in acids. These results will form the basis of later papers by other members of the laboratory staff.

being continuously renewed, the oxygen transported in this manner might be of the same order of magnitude as that which diffuses in the ordinary way. In most pipe systems, however, the concentration of colloidal ferric hydroxide is quite low and it seems improbable that its catalytic effect can be of more than very slight importance. The possibility of catalysis by accumulated $Fe(OH)_3$, and the impossibility of controlling or reproducing the convection currents which largely determine the rate of diffusion of oxygen, unite to throw doubt on the validity of the ordinary "beaker" corrosion tests as far as they are applied to corrosion by natural waters. The work of Speller in measuring the rate of corrosion when water flows through standard pipe coils marks a great advance in obtaining reliable data applicable to actual operating conditions.

"On the other hand, small variations in the acidity or alkalinity of the water, or moderate concentrations of neutral salts should have no direct effect unless they were themselves depolarizing agents for H_2, or affected the catalytic properties of the $Fe(OH)_3$ formed by the reaction. Very high concentrations of salt should tend to decrease corrosion by decreasing the solubility and increasing the viscosity of the solution, the latter factor tending not only to increase the thickness of the stationary film, but also to decrease the specific rate of diffusion of oxygen.

"The most important conclusion to be drawn, however, is that, since the limiting factor under these conditions is the rate of diffusion of oxygen to the metal, the composition or heat treatment of the iron or steel, or the presence of impurities, should not appreciably affect the results. While this may seem surprising, it is in entire accord with the best data on the subject—, as, for example, the A.S.T.M., under-water corrosion tests on various kind of sheet iron and steel (final report has not yet been made,) the careful tests of Richardson[1] on pure iron *vs.* steel, and the final tacit compromise in the prolonged wrought iron *vs.* steel controversy. The contrary impression has resulted partly from the results of accelerated tests in acid solutions, where composition does affect the results. Some rather erratic results with different kinds of iron or steel in natural waters are almost certainly caused by insufficient control of the important, but frequently unappreciated, variable, the rate of circulation of the water.

"It is, of course, possible by alloying iron with relatively large proportions of other elements—for example, silicon—to so far reduce its solution pressure that Reaction I is controlling even in natural waters and composition becomes of primary importance. This is not true, however, of the ordinary variations in composition of iron and steel used commercially."

"When iron is immersed in acid solution of a pH higher than about 4.5, appreciable amounts of hydrogen begin to appear, first merely as dissolved gas; but by the time a pH of 4 is reached, bubbles are usually evolved. If the iron is in contact with other metals or impurities of low hydrogen overvoltage, this evolution may begin at considerably lower acidities. As soon as the evolution becomes appreciable, and at all high concentrations of acid,

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[1] Trans. Am. Inst. Chem. Eng. 13, Part I, 64 (1920).

the rate of Reaction 3 becomes the controlling factor. This should be somewhat affected by the hydrogen-ion concentration, since this determines the "equilibrium pressure" of the polarizing film. The most important factor, however, is the hydrogen overvoltage of the metal and impurities present. Marked differences between samples of varying purity show up in this range, and these differences are responsible for many of the broad statements that certain forms of iron are more resistant to corrosion than are others.

"Certain other factors are important indirectly on account of their effect on hydrogen overvoltage—as, for example, temperature. A recent interesting paper of McInnes[1] shows that at low rates of gas evolution the overvoltage is determined by the amount of work which must be done against surface tension in forming the gas bubbles, and that it should accordingly increase in a vacuum and decrease under pressure. This leads to the surprising conclusion that vacuum should retard and pressure accelerate corrosion, and McInnes has checked this. Also, according to this theory, anything tending to decrease the average bubble size should also increase overvoltage, and this checks with recent observations in this laboratory (to be published shortly) that moderate rate of stirring tends to *retard* corrosion in acid solutions. Overvoltage is also apparently raised markedly by certain readily adsorbed materials such as arsenic[2] and formaldehyde[3] and their presence in solution correspondingly retards corrosion in acids.

The oxygen concentration, salt content, solution pressure of metal, etc. should have comparatively little effect on the rate of corrosion in acids.

"To summarize, the whole field of corrosion of iron by dilute aqueous solutions may be divided into three main regions of varying hydrogen-ion concentration, in each of which a different but comparatively simple reaction controls the rate of corrosion."

"The factors determining the rate of corrosion of the most electropositive element in any given combination are precisely the same as for a single metal —the rate at which the polarizing film of hydrogen is removed by Reactions 2 or 3 is still the limiting condition. In the case of most electronegative elements in contact with iron, the overvoltage is high enough to prevent the escape of appreciable amounts of hydrogen when in contact with natural waters, and in this case the limiting factor must again be the rate of diffusion of oxygen to the surface. In other words, the amount of corrosion will be determined by the *total area saturated with* hydrogen, but the loss in weight will all be concentrated on the iron portion of the surface, so that the rate of corrosion of the iron itself will be accelerated to an extent depending on the area of inert surface which it is able to keep saturated. Preliminary experiments in this laboratory indicate that the corrosion of iron in contact with copper in natural waters is accelerated to very nearly the extent predicted from the relative areas of the two metals. In view of this, relatively small areas of impurities of segregated materials could have but little effect. On

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[1] McInnes and Contieri: J. Am. Chem. Soc., 41, 2013 (1919).

[2] Friend: "The Corrosion of Iron and Steel", 211 (1911).

[3] Griffin: J. Ind. Eng. Chem. 12, 1159 (1920).

the other hand, where an iron pipe is almost completely covered by an inert conductor, such as mill scale or lead, the small unprotected areas should corrode with great rapidity, causing the deep pits characteristic of such conditions.

"There are, however, one or two notes in the literature which indicate more than normal acceleration by contact with a small piece of other metal. Thus, Walker,[1] in order to account for the marked accelerating action of a comparatively small area of platinum in contact with iron observed in some tests with "ferroxyl indicator,"[2] postulates an increased reaction rate between the oxygen and hydrogen at the platinum surface. This would be a convenient assumption since it would account for any observed amount of acceleration but does not appear to be tenable in view of the reasoning in a previous section which indicated that the rate of reaction, even at an iron surface, was much more than that required to take care of all the oxygen which could diffuse into the surface. Furthermore, this rate of diffusion could not be affected by the nature of the metal surface.

"As a possible explanation of Walker's observations, it was considered that the ferricyanide might have been acting as a depolarizer by oxidizing the hydrogen, especially at the platinum surface. On repeating the experiments, it was found that no appreciable acceleration could be observed qualitatively in the absence of ferricyanide, and that when ferricyanide was present, ferrocyanide was rapidly produced around both the platinum and iron surfaces, as shown by the color found in these regions when dilute $FeCl_3$ was poured on top of the jelly. Tests in the absence of oxygen also indicate that under these conditions, some hydrogen is evolved as such (dissolved) from the platinum surface, probably because of the increase in the potential of the corrosion reaction due to the maintenance of a low concentration of Fe^{++} plus the low overvoltage of platinum. The behavior and rate of corrosion in the two tests were quite different, and from the foregoing facts it must be concluded that the ferroxyl test, while very interesting, is not in any sense a reliable indication of what really happens in ordinary corrosion.

"In considering the rate of corrosion of electropositive elements, such as zinc, in contact with iron, the tendency to form hydrogen is so great, even in natural waters, that the overvoltage of one of the metals is likely to be exceeded and hydrogen evolved, even the natural-water range giving a greater rate of corrosion than that corresponding to the rate of diffusion of oxygen. Sodium is an excellent example of such a case, while zinc is probably just on the border line, and owes its pre-eminence as a protective material to this fact. More positive elements would corrode too rapidly with the evolution of considerable hydrogen, while less positive metals would not adequately protect a reasonable area of iron."

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[1] Mech. Eng. 23, 677 (1909).

[2] A neutral jelly containing ferricyanide and phenolphthalein indicators to indicate where iron goes into solution and where alkali is produced. See Friend: "The Corrosion of Iron and Steel", p. 248.

Whitman and Russell[1] say that "present opinion on the mechanism of the corrosion of iron and steel by natural waters can be broadly divided into two camps. The first is agreed that corrosion is initiated by a reaction of metallic iron and hydrogen ion, producing ferrous ion and nascent hydrogen. The other group centralizes on a colloidal explanation of the process and considers that hydrogen is not involved in natural water corrosion. The first position is presented by Wilson[2] in a paper which embodies several important advances over the views of earlier writers. Wilson divides the subject of submerged aqueous corrosion of steel into three fields—alkaline, natural water, and acid—and enumerates the controlling factors in each. The primary reaction in all cases is that between metallic iron and hydrogen ion.

$$Fe+2\,H^+=Fe^{++}+2H \qquad (1)$$

In alkaline water the rate of corrosion is limited by the low concentration of H^+. Since the nascent hydrogen is formed only slowly, it can readily be removed by oxidation by the dissolved oxygen in the solution to form water

$$2H+1/2\,O_2=H_2O. \qquad (2)$$

Reaction 1 speeds up as the H^+ is increased towards the neutral point, until it becomes faster than the depolarizing Reaction 2. Under these conditions the rate of corrosion is limited by the rate at which the polarizing film of hydrogen can be removed by oxidation, and Reaction 2 becomes controlling. Wilson further states that the speed of the depolarizing reaction is determined almost solely by the rate at which dissolved oxygen can diffuse into the metal surface, and it is practically independent of hydrogen-ion concentration and composition of steel within the limits of natural waters.

"Further increase in H^+ concentration results in the evolution of hydrogen gas, and the reaction

$$2\,H=H_2 \qquad (3)$$

proceeds in parallel with oxygen depolarization to remove the polarizing film of hydrogen. In this acid range overvoltage is an important factor because of its relation to gas evolution. The various colloidal theories which have been proposed agree that the function of oxygen in natural water corrosion is either to oxidize ferrous iron to ferric, which then corrodes the metal and is reduced to ferrous, or to oxidize the metal directly. Although the exact concepts of the different writers vary, they are in general agreement that hydrogen is not an essential part of the corrosion under these circumstances.

"Walker,[3] discussing the mechanism of corrosion when two metals are in contact, shows that a circuit is built up whereby the metal that is the anode goes into solution while hydrogen is deposited on the cathode. Thus iron in contact with zinc is protected and the zinc corrodes, while iron in contact with copper corrodes at a higher rate than if the copper were absent. Aluminium and other metals that rapidly form a protective oxide film do not exert the action exhibited by zinc.

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[1] Ind. Eng. Chem. **16**, 276 (1924).

[2] Ind. Eng. Chem. **15**, 127 (1923).

[3] Walker, Cederholm, and Bent: J. Am. Chem. Soc. **29**, 1251 (1907).

"For corrosion of steel in natural water, the increased rate due to contact with copper or other metals lower in the electromotive series should be due to the greater surface available for hydrogen depolarization by dissolved oxygen. Wilson points out that the overvoltage or specific catalytic properties of the second metal are not concerned unless conditions are such that hydrogen can be removed by gas evolution or by depolarization by oxidation from agents other than dissolved oxygen. Where dissolved oxygen alone is concerned, as with most natural waters, the rate of oxygen diffusion to the polarized surface is the main factor that determines the rate of depolarization and hence of corrosion.

"The effective area of the cathodic metal in accelerating corrosion is determined by the relative rates of hydrogen deposition and of oxygen diffusion. At any point where hydrogen is deposited more rapidly than oxygen can depolarize it, the area may be considered equivalent to an equal area of steel. This means that the total area for depolarization (area of steel plus effective area of other metal) determines the *rate of corrosion*, although the *actual corrosion* is localized on the steel alone.

"Since the hydrogen deposition depends on an electrochemical reaction, the factors that must be considered are (a) difference in potential between the metals, (b) conductivity of the liquid-metal circuit, and (c) rate of oxygen depolarization. It is clear that the distance over which acceleration can occur will be determined largely by the conductivity of the solution. It should be understood that a copper surface on which the rate of hydrogen deposition is lower than the potential rate of oxygen diffusion (because of insufficient electrolytic action) is not so effective as an equal area of steel.

"According to the foregoing viewpoint the effect of bringing a unit area of copper into "effective" contact with a unit area of steel would be to double the area for oxygen depolarization and hence to double the actual amount of corrosion occurring on the unit area of steel. Similarly, the result of copper-plating small areas of a piece of steel would be to localize the same total amount of corrosion on the uncoated areas, with a certain degree of pitting."

"The results show the same total rate of corrosion for bare steel as for the same area of steel when copper-plated over 75 per cent of its area. In the latter case this corrosion is localized on the steel alone, as is proved by the absence of any tarnishing on the copper surface and by the deeper corrosion of the exposed area of steel. The corrosion per unit area of exposed steel is therefore four times as great with the copper-plated specimens, since the same total corrosion is concentrated on one-fourth the area. It will be noted that protection of the copper apparently extends over greater distances than the 0.75 cm observed in beaker tests; this is probably due to presence of pinholes in the plated copper.

"These observations confirm the theory that the rate of corrosion is determined by the rate of oxygen diffusion to the metal surface where hydrogen is deposited. Hydrogen deposition in the first experiments occurred over the total surface of steel, and the oxygen diffusing in performed the dual function of depolarizing hydrogen and oxidizing the outer layer of rust from ferrous iron to ferric. In the experiments with copper-plated surfaces oxygen diffusing to the copper served only to depolarize hydrogen, while that diffusing to the steel oxidized both hydrogen and ferrous iron. In any event the equal corrosion obtained from the bare and plated samples demonstrates that under normal conditions the function of the copper surface is very simple and that oxygen diffusion to remove the hydrogen film is the controlling factor. These results cannot be reconciled with the colloidal theory proposed by Friend. Friend states his theory as to the mechanism of natural water corrosion as follows:

"In neutral solution, therefore, process No. 2 predominates (corrosion proceeds by catalysis, the catalyst consisting of a colloidal iron hydroxide) and the *rate of corrosion depends almost entirely upon sol formation.* (Italics are the authors'.)

"It is obvious that the "colloidal iron catalyst" does not exist on the surface of the copper, and therefore that Friend's theory cannot explain the fact that total corrosion is the same when steel surface is replaced by copper. (The authors do not believe that positive evidence of the catalytic effect of colloidal iron hydroxide on the corrosion of steel has yet been presented).

"The results of the beaker tests on the corrosion of steel in contact with copper and platinum agree with the concept of hydrogen depolarization. Wilson has pointed out the fallacy of applying the ferroxyl indicator test as a measure of natural water corrosion, since an additional depolarizer (ferricyanide) is introduced. The absence of any specific catalytic corrosion effects from platinized platinum in the beaker tests demonstrates that the process is controlled by oxygen diffusion rather than by a rate of chemical reaction."

Whitman and Russell draw the following conclusions from their experiments.

"1—Contact of steel with metals lower in the electromotive series sets up electrolytic action and increases the corrosion of the steel in natural waters. Since under these conditions the rate of corrosion is determined by the rate of hydrogen depolarization by dissolved oxygen, the accelerated corrosion of steel in contact with copper is due to the increased area available for depolarization.

"2—Depolarization of hydrogen on the steel surface is limited by the rate at which dissolved oxygen can diffuse from the liquid in to the surface. Hydrogen is deposited also on the adjacent copper surfaces, where it can be oxidized as fast as oxygen is supplied—i.e., just as rapidly as on the same area of steel surface. On portions of the copper at a greater distance from the steel, hydrogen deposits on the copper less rapidly than the potential rate of oxygen diffusion, owing to the increased resistance of the electrolyte in the liquid-metal circuit. These portions are less effective as depolarizers and the effectiveness decreases as the distance from the corroding steel becomes greater. The total effect of the copper is to increase the rate of corrosion of the steel proportionately to the increase in the "effective" area for depolarization. Increased conductivity of the solution permits the copper to act as a depolarizing surface at greater distances from the steel.

3—The older theories of the specific catalytic properties of metals as depolarizers, or of their effects in lowering over-voltage, have no bearing on the normal corrosion of steel in natural water at room temperature.

4—The results offer experimental confirmation of the electrolytic mechanism of corrosion and of Wilson's predictions as to the magnitude of the accelerated corrosion of steel in contact with lower metals.

5—The results cannot be explained on the basis of those theories of Friend[1] or Bengough and Stuart,[2] which involve direct oxidation of the metal or metal ion and which neglect electrolytic action."

The great difficulty about experiments on corrosion is the length of time ordinarily required for a single experiment. To make real progress we must devise a satisfactory accelerated test. I do not agree with Cushman and Gardner[2] in their statementthat "owing to the nature of corrosion it is probably true that no perfectly reliable acceleration test for corrosion resistance can be devised. Corrosion, in the natural process of rust formation, that is to say, in very slightly acid media, is a question of comparatively slow growth under special conditions, and any effort to hasten the action changes all the conditions of equilibrium, producing an entirely different order of phenomena."

While this statement may be right, it is a pure assumption at the present time and not a plausible one. Of course the conditions for the stability of a surface film will be different under atmospheric corrosion from those for immersion; but, if we can develop a satisfactory test for the matter, it will be a simple matter to introduce the modifications for atmospheric corrosion. While I cannot give an accelerated test now for corrosion in aqueous solutions, I can outline it. The first thing to do is to determine the voltage-current curve in the solution to be studied, measuring the anode potential, to determine whether, and under what conditions, the metal becomes passive. With that out of the way the accelerated test will be an electrolytic one. We shall have to determine: how high a current density is permissible; where the cathode should be placed; whether and when stirring is permissible; how often the solution should be changed; etc. A great deal of work will have to be done before we can write exact specifications for an accelerated test and we shall have to prove, beyond a peradventure, that the accelerated test can be relied on to give reliable results in every case. I feel sure, however, that this can be done, and that the eventual rapidity with which we can then accumulate data, will more than pay for the time spent in preliminary experiments. The most valuable thing that I learned from Ostwald was that it pays to spend an apparently inordinate length of time developing one's method of attack provided one is sure of working at a sufficiently increased speed later. Certainly the experience of the last twenty years' study of corrosion has demonstrated the futility of the haphazard method of attack.

I am sorry to say that Mr. Speller is rather sceptical as to the preceding paragraph. He doubts seriously whether the accelerated test of the future

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[1] Iron Steel Inst., (London), Carnegie, Schol. Mem. 11, 125 (1922).

[2] "Sixth Report to the Corrosion Research Committee of the Institute of Metals" (1923).

[2] "Corrosion and Preservation of Iron and Steel," 99 (1910).

will be electrolytic only or whether we are justified in using a higher electromotive force to carry the metal into solution than is natural to the kind of corrosion under consideration. This criticism is fundamental if sound, because it bars out any accelerated method of this type. There will be occasions, copper in bichromate solution for instance, where it will not be permissible to run up the current density; but that is already covered. It will also not be permissible to increase the current density to the point at which we do not get selective corrosion with a two-phase alloy; but there are no satisfactory data as yet to show at what point this occurs and I am quite certain that the corrosion can be accelerated considerably. Mr. Speller adds that "it seems from our study of the subject so far, that all the main factors should be included in an accelerated test in their right relation to each other. Very often sufficient acceleration will be obtained by keeping the oxygen concentration constant and keeping the test going continuously. This subject is now in the hands of sub-committees of the American Society for Testing Materials having to do with accelerated corrosion tests for ferrous and non-ferrous metals and should be considered very carefully before definite recommendations are made which might afterwards have to be recinded".

Speller and Kendall[1] have developed a special, accelerated test for corrosion in natural waters where the dominating influence is the content of dissolved oxygen. Since the corrosion is almost directly proportional to the dissolved oxygen content, it is possible to measure the amount of corrosion by measuring the amount of oxygen used. "Arndt[2] used an oxygen absorption method based on measuring the oxygen gas removed from moist air in which the samples of metal under observation were exposed in a closed vessel. While this is an approximation of atmospheric corrosion, it can not be applied to under-water corrosion. Moreover, in piping installations and service lines, the most important factor is the concentration of the dissolved oxygen. A measurement, then, of the decrease or drop in dissolved oxygen through any system becomes a measurement of the amount of corrosion in that system. This is manifested in a practical way by the early failure of portions of the system near the water inlet and the comparatively long life of other parts farther away. The dissolved oxygen is removed in the first lengths of pipe so that the pipe farther away is furnished with water almost free from dissolved oxygen. It would seem, therefore, that, by using an iron pipe of a convenient size and measuring the oxygen concentration in the water which was caused to flow through such a pipe, rapid and accurate measurement of the corrosion could be made.

"The main factors which influence corrosion aside from oxygen concentration are temperature, velocity of flow, composition of the water, and protecting influence of films of oxides or other matter formed on the surface of the metal. By keeping all the factors constant except the one to be measured, the influence of this one can be readily determined. Considering the number of varying factors entering into corrosion, it is very desirable to have a method of

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[1] Ind. Eng. Chem. 15, 135 (1923).
[2] Chem. Ztg. 24, 425 1078 (1910).

investigation by which tests can be made in a comparatively short time so that all other factors can be easily kept constant. This method we believe has fulfilled these exacting requirements. It is quite evident, of course, that the method does not apply to either decidedly alkaline or acid solutions; but the great bulk of natural waters falls within the range of pH 5 to pH 11, and it is in this range[1] that oxygen concentration is the dominating factor. . . .

"An apparatus was constructed consisting of a coil about 18" in diameter of 200 ft. of 1/4" black pipe placed within a drum. The coil was tapped every five feet up to 30 ft. and then at 40, 50, 75, 100, 150, and 200 ft. In order to maintain constant time of contact at different velocities, the length of pipe was varied. For example, at a velocity of 1 ft/sec. the water had a time of contact of fifty seconds when it was passed through 50 ft. of pipe. When the velocity was raised to 2 ft./sec. the water was passed through 100 ft. of pipe. In this way the only variable at any given temperature was the velocity. A gas heater was connected with the apparatus so that the water could be heated to any desired temperature. At the higher temperatures, to maintain an even temperature throughout the entire system, steam was introduced into the drum. All connections and pipes from the gas heater to the coil and also the cooling coils and connections were of brass. At the entrance to the coil a small amount of water was by-passed through a cooling coil and the dissolved oxygen content determined by the standard Winkler method.[2] The water, after passing through the experimental coil, was cooled to normal temperature and its oxygen content determined. All the samples were cooled under pressure so that the gas would not separate when the pressure was lowered. The initial pressure was varied from 40 to 75 lbs. Under no condition was the exit pressure less than 10 to 20 lbs. . . . To ensure that the coil was representative of actual pipe installations, 200 ft. of 1/4" pipe was laid out in a straight line and the pressure drop measured at taps corresponding to those in the coil. The coil did not increase the frictional loss appreciably except for the last two lengths.

After this series of tests were run, the 1/4" pipe was replaced by 1/2" and later by 3/4" pipe. Because of the large volume of water required for obtaining high velocities on the two latter sizes of pipe, it was found necessary to insert an auxiliary cooling coil consisting of 30 ft. of copper pipe at the discharge from the experimental coil. This cooled all of the water at a temperature of 50° to 110°F, depending on the working temperature. The discharge was then split, part passing through another cooling coil which brought the temperature down to between 40° and 60° F. It was then sampled for dissolved oxygen and the remainder wasted. Each rate of flow was set by a stopwatch. Particular pains were taken to hold the temperature absolutely constant throughout the entire length of the coil. The condition of the suface of the test pipe was determined at frequent intervals to make sure that the rate of corrosion had not changed materially by reason of adhering rust films."

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[1] See Wilson: Ind. Eng. Chem .15, (1923).

[2] American Public Health Association, p. 65 (1920).

Speller considers that this new method of measuring corrosion is especially applicable to the investigation of corrosion factors such as velocity and film protection. He states that tests of the rate of corrosion may be made in a few minutes by measuring the drop in oxygen. This method should be accompanied by long time tests in which the loss in weight and depth of pitting may be determined.

In this report I have made no attempt to cover the literature of corrosion. I am hoping that that will be done by Professor Fink at Columbia. I have made no attempt to account for all the phenomena. I could not have done it if I had wished to. A great deal of work will have to be done by many before we shall be able to say that we have an adequate knowledge of corrosion. I have made an attempt—and I hope a successful one—to show that the contention of Bengough and Stuart, that the electrolytic theory of corrosion is inadequate, is certainly premature and probably inaccurate. I concede that they have made out a very good case against the distinctly one-sided presentation of the theory by Cushman and by Lambert; but Bengough and Stuart did not rise to the occasion. Instead of pointing out that the facts could be accounted for satisfactorily by a broader form of the electrolytic theory of corrosion, which was to be found in the literature, they adopted the hypothesis of a direct, non-electrolytic corrosion, and that seems to me a distinct step backward. I do not believe that that will prove a satisfactory working hypothesis in the study of the properties of surface films, which both sides admit to be the fundamental problem before us.

Cornell University.

ESTERIFICATION IN PRESENCE OF SILICA GEL[1]

BY C. H. MILLIGAN, J. T. CHAPPELL AND E. EMMET REID

It is well known that esterification in the vapor phase is catalyzed by certain oxides. Sabatier and Mailhe[2] studied the effect of titania and thoria on a mixture of equivalent amounts acetic acid and ethyl alcohol and, in the most favorable cases, obtained 67% esterification which was very close to Menschutkin's value[3] of 66.7. It has been assumed by Sabatier and Mailhe[4] that the limit in gas phase reached in the presence of these catalytic oxides would be the same as that in the liquid phase. They found about 70% esterification at 300° and attributed the slightly higher value to the higher temperature since Berthelot had found 65.6% at 100° and 67.3% at 200°. This view seems to have been commonly accepted, particularly as no measurements are on record of the equilibrium in the gas phase.

Berthelot and Péan de Saint-Gilles[6] made several attempts to measure the equilibrium in the gaseous phase but did not succeed on account of the extreme slowness of the reaction. In parallel experiments in which equivalent amounts of alcohol and acetic acid were heated 10 hours at 200° there was 65.2% esterification in the case in which the volume of the tube was 2.6 cc. per gram of mixture and only 10.0% where this volume was 1351 cc. In another experiment in which the volume was 1562 cc. the esterification was only 49.0% after 458 hours at 200°. Starting from the other end, they heated ethyl acetate with 2 equivalents of water at 200° and found 11.5% hydrolysis in 0.5 hour where the volume was 2.3 cc per gram but with the volume 476 cc. the decomposition of the ester was "insensible" in 142 hours. These experiments demonstrate the extreme slowness of the reaction in the gaseous phase and, by contrast, serve well to show the enormous accelerating influence of the catalytic oxides.

They ran two series of experiments[6] in which the volume per gram of mixture was varied and with equivalent amounts of ethyl alcohol and acetic acid at 200° obtained the following results:

Time hours	Vol to 1 g.	% Esterification
22	5.4	66.4
77	37.0	72.3
77	53.0	76.0
10	2.6	65.2
22	5.3	66.4
22	8.3	66.8
22	21.2	71.7
22	24.4	72.9

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[1] Contribution from the Chemical Laboratory of Johns Hopkins University.

[2] Sabatier and Mailhe: Compt. rend. 152, 358, 494, 669 and 1044 (1911).

[3] Ann. 195, 334 (1879), Ann. chim. phys. (5) 20, 289; 23, 64 (1880).

[4] "Catalysis in Organic Chemistry," p. 277 (1922).

[5] Ann. chim. phys. [3] 66, 54 (1862).

[6] Ann. chim. phys. [3] 66, 59 (1862); 68, 239 (1863).

They conclude (p. 243) that increase of volume favors the combination of acids and alcohols and enfeebles the inverse action of water on the esters.

It appears then, that if the limit of esterification could be measured in the gaseous phase, it would be found to be high, apparently very much higher than the 66.5% found for the liquid phase. With silica gel as catalyst we have obtained esterification up to 89.6%, the percentage depending on the time of contact, but have no reason to think that equilibrium has been reached. In this system in the liquid phase, esterification goes on 4 times as rapidly as saponification, in the vapor phase this ratio is apparently much higher. The 89.6% esterification which we have reached corresponds to a ratio of 74 and the true ratio is probably higher yet.

Recently Edgar[1] has measured the limit for ethyl alcohol and acetic acid by a distillation method and his preliminary results indicate a limit well above 90%. Perhaps the excellent yields of esters obtained by Bodroux[2] and the remarkable results obtained in plant processes for ethyl acetate from very dilute solutions of acetic acid as described by Whitaker[3] may be connected with the more favorable location of the equilibrium point in the vapor phase.

We find silica gel to be more active in esterification than either thoria or titania is said to be.

The Present Investigation

The experiments in Tables I and II were carried out by C. H. Milligan in 1921 and reported at the Rochester meeting of the Society; those in the later tables are by J. T. Chappell, using the same furnace and same methods but with different materials and standard solutions and working a year later.

Apparatus and Methods. The catalyst tube was pyrex glass 18 mm. inside diameter. The catalyst, 100 g. of silica gel,[4] occupied 450 mm. of this tube of which the portion in the furnace was 570 mm., the vacant space being nearly all at the forward end to allow the gases to come to temperature. This end of the tube projected 100 mm. out of the furnace portion being surrounded with asbestos and heated by an extra coil wire, thus serving as a volatilizing chamber for the liquid mixture. The electric tube furnace was automatically controlled and kept the desired temperature within ±1° for a week at a time.

The mixture of exactly equivalent amounts of pure acetic acid and absolute alcohol was admitted through a needle valve dropping device which could be regulated to admit the liquid at so many drops per minute. By weighing a number of the drops the rate could be determined. All rates are stated in number of cubic centimeters of mixed vapors at the temperature of the furnace. By turning the regulating screw this rate could be set from 4 drops to 160 per minute or from 40 cc. to 1600 cc. of vapors per minute. As the free space in the catalyst chamber was 82 cc. the time each molecule was in this space can be calculated. The amount of esterification was determined by

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[1] Professor Edgar has kindly let us see some of his results in advance of publication. See J. Am. Chem. Soc., **46**, 64 (1924).

[2] Compt. rend. **156**, 1079 (1913); **157**, 1428 (1913).

[3] Chem. Met. Eng., **28**, 108 (1923).

[4] For which we are indebted to Professor Patrick.

titrating the free acid in a weighed sample of the condensate. To check the figures thus obtained, the ester was determined in a number of samples by saponification. The values obtained in the two ways checked very closely.

In Table I are given a number of analyses of successive samples of the condensate when the furnace was set at different temperatures and the rate of the vapors varied.

TABLE I

No.	Temp.	Rate cc. per min.	Time in Furnace sec.	Percent Esterification
1	150°	40	123	89.6
2	"	66	74	82
3	"	"	"	85
4	"	"	"	85
5	"	"	"	87
6	"	120	41	68.7
7	"	255	19	43
8	250°	89	56	77.5
9	"	177	28	72.5
10	"	"	"	74.0
11	"	"	"	76.0
12	"	"	"	76.0
13	"	"	"	76.0
14	"	"	"	76.4
15	"	290	17	69.0
16	"	"	"	71.0
17	"	380	13	64.0
18	"	"	"	64.6
19	"	"	"	69.5
20	"	"	"	70.0
21	"	630	8	57.5
22	"	"	"	60.7

It appears that the percentage of ester formed at a given temperature is closely related to the rate at which the mixture is passed over the catalyst.

To account for the high percentages of esterification obtained our first supposition was that water was being retained by the gel, the equilibrium being shifted according to the mass law by diminishing the concentration of that constituent. For 66% esterification the partial pressure of the water vapor would be 253 mm. and it was thought that the gel might absorb a considerable amount of water at this concentration.

Quantitative experiments were made to determine the amount of water taken up by the gel, at several temperatures, from air containing this amount of water vapor. A weighed sample of silica gel was heated in a U-tube in an oil bath to the desired temperature and air which had bubbled through water at 72° was drawn over it. This was continued to constant weight.

The amount of water retained by silica gel at 253 mm. partial pressure is:
At 150° 9.27%; at 200° 7.25%; at 250° 5.38%.

The sample of gel used was the commercial gel and had become saturated with moisture under usual atmospheric conditions and contained 17.95% of water. When heated up to the temperature at which it was used, a part of this water was given off. When it was used at a higher temperature and then at a lower, some water would, of course, be taken up and might account for the high esterification figures, at least till it had acquired the proper amount of water.

In order to test this a run was made in which the mixture of acid and alcohol was passed continuously for 108 hours at 150° in which time 420 g. of the mixture passed over the gel and about 50 g. of water was set free, or 5 times the total water content of the lot of gel at 150°.

During this run the rate was varied from time to time and samples taken at the different rates, but not till the rate had remained constant long enough for conditions to become constant. The results are given in the table below:

TABLE II

Esterification at 150°

No.	Rate cc. per min.	Time in furnace sec.	Amount that had passed through, g.	Percent of esterification
1	82	60	17	76.5
2	82	60	40	76.6
3	82	60	100	74.2
4	82	60	102	75.0
5	40	123	115	85.0
6	82	60	125	74
7	100	44	135	65.5
8	82	60	150	74
9	82	60	—	72
10	82	60	200	79.6
11	40	123	—	89.6
12	82	60	300	70
13	50	98	305	83
14	82	60	400	75.2
15	120	41	420	60

Most of the samples were small but No. 12 and 14 were each from 100 g. of the condensate. It appears from this long run that when the rate is the same, the percentage of esterification is nearly the same. At very slow rates the percent of esterification is very high, even approaching 90%.

On account of the length of the run and the large amount of water involved the excess of esterification cannot be accounted for by supposing retention of water by the gel. The high values are all the more remarkable when the water content of the gel is considered. If we think of the alcohol and acid as being in solution in the water in the gel we must have a rather dilute solution, even taking into account the displacement of a part of the water by alcohol and acid. Under constant conditions the amount of water in the gel is fixed, yet it is the amount of the water and not the individual molecules of water that is fixed. They are free to go and come and to react as other water molecules.

TABLE III

Esterification at various temperatures.

No.	Temp.	Rate, cc.	Time, sec.	% Esterification
1	148	84	57	44.5
2	175	56	86	73.9
3	"	89	54	57.8
4	"	103	47	51.3
5	197	58	82	78.5
6	200	89	54	71.3
7	222	62	78	76.4
8	230	100	48	54.9
9	245	119	40	70.6
10	275	103	46	68.6
11	320	136	35	63.0

TABLE IV

Esterification at 175°

No.	Rate, cc.	Time, sec.	% Esterification
1	56	86	73.8
2	79	61	61.0
3	89	54	57.8
4	93	51	52.7
5	103	47	51.3
6	107	45	47.9
7	112	43	48.4

TABLE V

Esterification at 200°

No.	Rate, cc.	Time, sec.	% Esterification
1	4.9	975	84.4
2	20	244	81.3
3	35	139	80.4
4	38	125	80.6
5	44	108	79.1
6	49	99	77.3
7	54	87	77.4
8	59	81	77.8
9	88	54	71.3
10	118	41	64.8
11	138	35	53.7
12	197	24	39.5

At 200° there was a slight diminution of activity of the gel with time as is shown by two runs at two constant rates:

TABLE VI
Esterification and Time of use.

Time, days	0	7	9	14	15
Rate, 38 cc.	83.9	——	80.7	79.4	78.3
Rate, 44 cc.	81.0	79.7	——	——	76.6

In a given run when conditions are kept constant the percentage of esterification is nearly, but not quite constant as is shown by the following run.

TABLE VII
Variation of Esterification

Temp. 175° Rate 107 cc.

Time, min.	289	297	362	369	377	449	456	464	540	547	552
% Esterification	52.8	52.4	52.1	52.1	51.9	51.5	51.2	51.5	51.2	53.3	51.2

In the figure the percentage of esterification is plotted against the time the vapors remained in the furnace. The numerals on the curves refer to the tables from which the figures are taken.

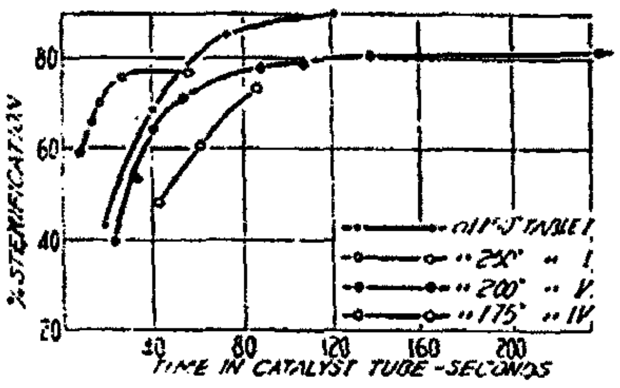

FIG. I
Percentage Esterification Against Time in Catalyst Tube

From this it is apparent that high temperature makes for rapid esterification; that the percentage of esterification increases with the time up to a certain point where it becomes nearly constant as if a limit were being approached but this apparent limit is lower for higher temperatures. From observations of Brown and Reid[1] only 16% of ethyl alcohol is decomposed by silica gel at 360°, when passes at a comparable rate, from which it is probable that it would break up very slightly at 200°, or even at 250°. It is possible that the ethyl acetate may be less stable in the presence of silica gel and may decompose with the re-formation of acetic acid. In a 9 hour run, the products of collected weighed 473. and the reactants put in, 52 g., the loss being too great to be accounted for by evaporation.

In both series of experiments commercial silica gel was used but the first sample, Tables I and II, appears to have been considerably more active than the second. After 27 days of use the gel was quite black.

One run was made at 200° in which 2 equivalents of alcohol were used to 1 of acid. The results are given in Table VIII.

TABLE VIII
Esterification at 200°, 2 equiv. alc.

Time in sec.	62	49	39
% Esterification	89.9	82.5	75.5
do for 1:1	77.6	74.7	71.5

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[1] Paper to appear in a subsequent number of this Journal.

The figures in the last line are taken from the curve for 200° in Figure 1. The excess of alcohol speeds up the esterification considerably.

Comparison of Catalysts

Taking the results of Sabatier and Mailhe[1] we may make a rough comparison of silica gel with their catalysts. They ran 0.2 mol of the mixture per hour which would mean 236 cc. of vapor per minute at 150°. Their results and ours are brought together in table below.

TABLE IX
Comparison of Catalysts.

Temp.	Rate	% Esterification		
		Thoria	Titania	Silica Gel
150°	236 cc.	11	20	43
170°	248	26	—	—
230°	277	45	60	—
250°	290	—	—	69

Summary

Silica gel has been found to be an excellent catalyst for esterification, better than thoria or titania. The percentage of esterification attained depends on rate of passage of the vapors, being about 90% for slow rates at 150°. There is no indication that the limit has been reached but this limit must be far higher in the vapor phase than in the liquid.

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[1] Sabatier and Mailhe as quoted by Sabatier: "Catalysis in Organic Chemistry," 278 (1922).

Baltimore, Md.

REACTIONS IN PHOSGENE SOLUTION. I.

BY ALBERT F. O. GERMANN

That phosgene is an extremely active compound is attested by the fact that the great majority of references to it[1] describe its use in some synthetic process. On the organic side, phosgene has been shown to be particularly reactive, and while the particular direction of its reaction with a given compound may vary much with the precise conditions of temperature, concentration, etc., in general, to use the words of Kühn[2], "the known reactions of phosgene proceed in two directions; in the first case they depend on the affinity of chlorine for atoms of hydrogen or of a metal in amines, hydrocarbons, metallo-organic compounds, and compounds containing the hydroxyl group; in the second they depend on the tendency of phosgene to be converted into carbonic acid in the action on aldehydes, ketones and acid amides, while the carbonyl oxygen of these compounds is exchanged for chlorine." Kühn then describes a new type of reaction in which "phosgene is capable of lifting the bond between carbon and tertiary amine nitrogen; the valences thus freed are satisfied by means of the phosgene parts, CO and 2Cl. This reaction has much resemblance to hydrolysis, and may have some connection with the ionizability of phosgene in solutions."

The work of Beckmann and Junker[3] throws some light on the question as to whether phosgene yields conducting solutions. Molecular weight determinations using phosgene as ebullioscopic liquid showed that acetic and benzoic acids dissolve in this solvent with the formation of double molecules, while the anhydrides of these acids dissolve as simple molecules. Since this behavior is recognized as a property of non-ionizing solvents, phosgene is classed with these. The dielectric constant has apparently not been determined, nor has anyone tried to electrolyze phosgene solutions. (See page 885).

As a solvent for inorganic compounds, Beckmann and Junker found phosgene to be very poor. Red phosphorus, arsenic, arsenious oxide, boric oxide, antimony, bismuth, stannous chloride, selenium and its chlorides, sulfur, sodium, potassium, calcium, thiocyanates, sulfides and sulfates of the alkalies and alkaline earths, zinc chloride, ferric chloride, ferric sulfate, chromic chloride, mercuric chloride and iodide, the chlorides of copper, lead chloride and chromate and silver chloride were all found to be insoluble. On the other hand they found iodine, iodine trichloride, the chlorides of antimony and the chlorides of sulfur soluble.

John Davy,[4] who discovered phosgene in the course of the controversy about the nature of chlorine, made a number of observations concerning its chemical behavior; its condensation with ammonia, and its action upon potassium, tin, zinc, antimony and arsenic when these are heated with the gas, forming chlorides of the respective metals and carbon monoxide.

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[1] Bibliography. Berolzheimer: J. Ind. Eng. Chem., 11, 263 (1919).

[2] Ber., 33, 2900 (1900). See also Hofmann: Z. angew. Chem., 21, 1986 (1908).

[3] Z. anorg. Chem., 55, 371 (1907).

[4] Phil. Trans., 102, 144 (1812); Nicholson's Journal, 30, 28 (1811).

Baud[1] found that phosgene readily dissolves anhydrous aluminium chloride, and that the solution yields various phosgenates. He identified three of these. Following this work, Bartal[2] investigated the solubility of the other halides of aluminium; he found the fluoride insoluble; the bromide was converted to chloride, with the production of carbonyl chlorobromide; the iodide reacted violently with the phosgene, yielding free iodine and a complex aluminium compound.

Besson[3] made a series of observations on phosgene reactions. He found that hydrogen bromide reacted above 200° C., to give traces of carbonyl bromide. Hydrogen iodide dissolved abundantly in phosgene cooled with ice and salt; but after a certain concentration was reached, a violent reaction occurred, yielding a quantity of iodine; using methyl chloride as a cooling bath, solution of HI proceeded regularly; but when the tube containing this solution was sealed off, and was left for several hours at a temperature several degrees below zero, a considerable quantity of iodine separated, and the tube contained an equivalent quantity of carbon monoxide. Phosphonium bromide reacted in the cold; rapidly at 50°C.; carried out in a sealed tube, very high pressures resulted, and hydrogen chloride, hydrogen bromide, solid and gaseous phosphine, and carbon monoxide were formed. Phosphonium iodide reacted slowly at zero, yielding hydrogen chloride, carbon monoxide, phosphorous, and iodides of phosphorous. Phosphine was without action. Hydrogen sulfide gave carbon oxysulfide at 200°. Hydrogen selenide gave hydrogen chloride, carbon monoxide and selenium at 200°. Selenium heated with phosgene at 230° gave carbon monoxide and selenium dichloride.

The Chemical Warfare Service has measured the vapor tension of solutions of hydrogen chloride in phosgene[4].

In contrast with the general insolubility of inorganic compounds in liquid phosgene, organic compounds are, as a class, readily soluble. This fact undoubtedly is partly responsible for the readiness with which organic compounds enter into reaction with it. As an acid chloride one would expect it to be reactive, and as a derivative of carbonic acid one would expect it to be a good solvent for carbon compounds. That phosgene is fundamentally as reactive with inorganic compounds is evident from the results of numerous investigations working at elevated temperatures, where the speed of reaction is much accelerated. Nuricsan[5] passing phosgene over heated metallic sulfides, prepared carbon oxysulfide; the preparation was especially successful with cadmium sulfide at 270°C. Chauvenet[6] using the same method converted oxides and sulfides into anhydrous chlorides. Barlot and Chauvenet[7] extended the method to phosphates and silicates, using temperatures ranging

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[1] Compt. rend., **140**, 1688 (1905).

[2] Z. anorg. Chem., **55**, 152 (1907); **56**, 49 (1907).

[3] Compt. rend., **122**, 140 (1896).

[4] Edgewood Arsenal Chemical Laboratory Report No. 223; see also W. M. Schaufelberger: Stanford University Thesis, 1920.

[5] Ber., **24**, 2967 (1891).

[6] Compt. rend., **147**, 1046 (1908); **152**, 87, 1250 (1911).

[7] Compt. rend., **157**, 1153 (1913).

from 350° to 1400°. Baskerville[1] describes a method for opening up acid insoluble minerals based on the great reactivity of phosgene at temperatures of 450° and above. Milligan, Baude and Boyd[2], working at Edgewood Arsenal, found they could utilize the waste phosgene in the tail gas from the condensers by passing the gas over a mixture of arsenious oxide and carbon at temperatures above 175°, the carbon acting as catalyzer, and arsenic trichloride being quantitatively formed.

Delépine and Ville[3] say that liquid phosgene free from chlorine, compressed in iron cylinders, will not attack iron, but will attack iron rust, forming ferric chloride, some of which dissolves in the phosgene. Schützenberger[4] attempted to catalyze the carbon monoxide chlorine reaction with platinized asbestos; the method was not successful because the nascent phosgene or the mixed gases destroyed the catalyst, forming volatile platinum carbonyl chlorides. Hamor and Gill[5] were able to synthesize the mineral phosgenite, $PbCO_3.PbCl_2$, by passing phosgene over lead hydroxide heated to 170°. Dixon's attempt to prepare carbonyl thiocyanate[6] by a reaction between metallic thiocyanates and phosgene yielded solutions of the compound, but he was unable to get the pure substance. Germann and Jersey[7] have reported the formation of molecular compounds between phosgene and chlorine, and between phosgene and boron trifluoride at very low temperatures. Paternò and Mazzucchelli[8] have measured the vapor tension of the solution formed by saturating phosgene with chlorine at -15°C., from -15°C. to $+40$°C.

The present investigation was undertaken in order to clear up certain points about the behavior of liquid phosgene, with particular reference to its free chlorine content, and the activity of its combined chlorine. Phosgene is dissociated into chlorine and carbon monoxide by ultraviolet light, as has been shown by Weigert,[9] by Coehn and Becker[10], and by Berthelot and Gaudechon;[11] and also by heat, as shown by the studies of Bodenstein and Dunant[12] Harak,[13] Atkinson, Heycock and Pope,[14] and others. According to the measurements of Atkinson, Heycock and Pope, which are the most complete, and probably the most reliable published, phosgene is appreciably dissociated by heat at temperatures above 200°, the degree of dissociation reaching nearly 20% at 400°, and 50% at 500°. This would seem to indicate that the reactivity of phosgene at temperatures above 200° may be due to the presence of free carbon monoxide and chlorine. As a matter of fact, most of the reactions

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[1] Science, 50, 443 (1919).
[2] Ind. Eng. Chem., 12, 221 (1920).
[3] Bull. 27, 288 (1920).
[4] Compt. rend., 66, 666 (1868); Bull. (2), 10, 188 (1868); Ann. chim. phys., (4), 21, 350 (1872).
[5] Am. Jour. Sci., (4), 47, 430 (1919).
[6] J. Chem. Soc., 83, 84 (1903).
[7] Science, 53, 582 (1921).
[8] Gazz. chim. ital., 50, I, 30 (1920).
[9] Ann. Physik., 24, 243 (1907).
[10] Ber., 43, 130 (1910).
[11] Compt. rend., 156, 1243 (1913).
[12] Z. physik. Chem., 61, 437 (1908).
[13] Thesis, Berlin, (1909).
[14] J. Chem. Soc., 117, 1410 (1920).

described above, taking place at elevated temperatures, may be carried out successfully by substituting for phosgene an equimolecular mixture of carbon monoxide and chlorine, as has been shown, among others, by Riban[1] and by Matignon and Delépine[2].

The work of Weigert[3] on the influence of light on the phosgene equilibrium loses most of its value because he enclosed his gas in a glass container, instead of quartz. Coehn and Becker[4], using ultraviolet light, found that phosgene is appreciably dissociated when exposed in quartz vessels; but there is no dissociation when exposed in glass vessels; these results were obtained by direct measurement of the resulting carbon monoxide, after absorbing the chlorine and unchanged phosgene in caustic potash. Berthelot and Gaudechon[5] got entirely similar results, but estimated the amount of dissociation by the soiling of a mercury meniscus by chlorine resulting from the dissociation; this required less than five seconds of exposure to ultraviolet light when the gas was in quartz, eighty seconds in uviol, and in ordinary glass no soiling was perceptible after two hours of exposure. The following statement by Berthelot and Gaudechon is surprising, in view of the fact that no change in volume occurs when the chlorine formed during dissociation is absorbed by mercury (in quartz): "En présence de mercure qui fixe le chlore, la décomposition continue et le volume se réduit peu à peu à moitié." Of course, the volume remains constant.

The evidence seems to be that reactions involving phosgene at temperatures below 200°, certainly up to 100°, carried out in glass containers, are not complicated by the presence of chlorine. Pure mercury in contact with pure liquid or gaseous phosgene is not soiled, unless the temperature is raised to near the critical point (178°); at this temperature the reaction is slow, but unmistakable.

Atkinson, Heycock and Pope[6] question the accuracy of the measurements of Bodenstein and Dunant[7] on the thermal dissociation of phosgene because the free chlorine was determined by passing the gas through an acid solution of potassium iodide, and titrating the liberated iodine with thiosulfate; the work of Besson[8] showed that pure hydriodic acid reacts rapidly with phosgene in the cold, and Delépine[9] has pointed out that phosgene liberates iodine from sodium iodide solution if the concentration of the latter exceed 0.1%. The Chemical Warfare Service recommends passing phosgene gas through tubes containing a mixture of potassium iodide and sodium thiosulfate in order to free the gas from traces of chlorine. My experience with this method indicated that either the phosgene used contained large amounts of chlorine, or that the method was not reliable.

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[1] Bull. 39, 14 (1883); Compt. rend., 157, 1432 (1913).
[2] Compt. rend., 132, 37 (1910).
[3] Ann. Physik, 24, 243 (1907).
[4] Ber. 43, 130 (1910).
[5] Compt. rend. 156, 1243 (1913).
[6] J. Chem. Soc. 117, 1410 (1920).
[7] Z. physik. Chem. 61, 437 (1908).
[8] Compt. rend 122, 140 (1896).
[9] Bull. 27, 283 (1920).

As a test, several grams of potassium iodide were sealed in a tube with a quantity of liquid phosgene, and the tube placed in a case where only diffused light reached it. After only a few days, the solution acquired the pink color of dilute permanganate solution, the color of dissolved iodine; and now, after eighteen months, the tube contains a quantity of large crystals of iodine, and the color is a deep claret. The reaction evidently does not depend on the presence of free chlorine.

To dissipate a lingering doubt on this score, however, the following experiment was tried. A generous sample of potassium was distilled into a carefully dried, evacuated tube, and the side tube, serving as retort, was sealed off. The sample, thus prepared, consisted of two principal portions: one where the violet vapors had deposited as a violet sublimate on the cool walls of the receiver, and the other where the silver white liquid metal had flowed down the tube, and frozen along the way. A carefully fractionated sample of phosgene was condensed in the tube, and it was sealed off. After twelve months of repose in the dark, no change had taken place in the brilliant luster of the metal, which I interpreted as evidence of the entire absence of chlorine. For, although dry chlorine does not react with potassium, Cowper[1] found that, when dry chlorine was admitted to bright potassium, the metal "at first remained bright, but slowly became covered by a film of a rich purple color. This is no doubt the subchloride described by Rose[2]."

At the end of twelve months, the tube was brought out and exposed to bright August sunshine for a few hours. During this brief period those portions of the bright potassium not covered with liquid phosgene, and some parts of the surface adhering to the glass, became covered with a film of a rich purple color, evidently the same substance described by Cowper in his experiments with chlorine. However, that part of the potassium covered by liquid phosgene remained bright, as well as some of the surface adhering to the glass. Since it was shown in two independent investigations[3] that those wavelengths capable of decomposing phosgene are screened off by ordinary glass, the effect of free chlorine in producing the reaction may be eliminated. If we assume that certain wavelengths capable of traversing glass act catalytically at the surface of the potassium to bring about the reaction, all the phenomena observed can be explained, if we assume, in addition, that phosgene absorbs the active wavelengths. There is only partial absorption in the case of phosgene vapor (under less than two atmospheres pressure at room temperature); but liquid phosgene absorbs them completely when presented in a thick enough layer. The formation of the purple film on the surface of the metal next the glass occurs only where the metal had become separated from the glass sufficiently for a film of phosgene to penetrate between them.

A knowledge of the absorption spectrum of liquid phosgene would undoubtedly help to clear up the phenomena observed, but no information seems

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[1] J. Chem. Soc., 43, 153 (1883).

[2] Pogg. Ann., 120, 15 (1863).

[3] Coehn and Becker: Ber. 43, 130 (1910); Berthelot and Gaudechon: Compt. rend. 156, 1243 (1913).

to be available along this line. At any rate, there seems to be no doubt that phosgene gas passed over solid potassium iodide yields a product, which while it may be chlorine free, certainly contains free carbon monoxide. The use of powdered antimony is to be preferred for the removal of free chlorine.

The behavior of the metals towards liquid phosgene is, in general, the same as that of potassium. In diffused light zinc, copper, and aluminium, in the form of bright foil, when exposed to the action of liquid phosgene, remain bright. It was to be expected that aluminium would dissolve, because aluminium chloride is soluble in liquid phosgene. The explanation at once suggested is that the protecting oxide film is sufficiently resistant to withstand the action of the solvent.

To determine this point, I tried the action of amalgamated aluminium. This involved special procedure, for the sample was so active, when amalgamated, that corrosion was well advanced before it could be dried, enclosed in a tube, the tube sealed to the apparatus, and evacuated. Carefully cleaned aluminium foil was covered with distilled water in a test tube, and a few drops of mercuric chloride added. As soon as the surface was coated with mercury, it was washed rapidly with distilled water, and then carbon tetrachloride was poured in until all the water was displaced. The amalgamated metal was then transferred to the trial tube along with enough carbon tetrachloride to cover it, the tube was sealed to the apparatus, the carbon tetrachloride was boiled away by evacuating with the water-suction pump, and, after thorough rinsing with phosgene, a sample of liquid phosgene was introduced by distillation, and the tube sealed off.

Prepared in this way, solution proceeded rapidly, carbon monoxide was evolved, and soon only a droplet of mercury remained. Amalgamated copper and amalgamated zinc, on the other hand, were not attacked—their chlorides are insoluble.

The effect of sunlight on the bright foil—not amalgamated— was startling; there was only slight surface corrosion of the zinc and copper, as was the case with potassium; but the aluminium reacted rapidly, showing lively effervescence due to evolution of carbon monoxide, which stopped when removed from the direct sunlight. As the reaction proceeded, the solution developed a yellowish brown color (due to iron as chloride), which affected the rate of reaction, so that after a time effervescence practically ceased; this effect seems to have been caused by the absorption of the active wavelengths by the colored solution. The thickness of liquid phosgene that had to be traversed by light in this experiment was about one fourth as great as in the experiment with potassium, which may account for the greater activity of the light in the present experiment. Iron present as impurity in the aluminium also reacted, yielding a yellowish brown solution, a darker deposit on the walls of the tube, and a dark brown residue. This residue, when heated carefully in the neighborhood of 200°, suddenly swells up, and yields a quantity of phosgene; when the temperature is raised still higher, the product fuses to the glass, and appears dark red by transmitted light, which seems to justify the conclusion that the substance is anhydrous ferric chloride, which must have been present as a slightly soluble phosgenate.

The formation of ferric chloride from iron and phosgene was unexpected, since the experiments of Delépine and Ville[1] on this subject were negative. Whether the presence of aluminium favored the reaction, or whether sunlight was a determining factor, has not been determined: nor has any study been made of the system ferric chloride—phosgene.

Magnesium is inert towards liquid phosgene; chlorine dissolved in phosgene does not attack magnesium; this is in harmony with the action of liquid chlorine on magnesium[2]. Since aluminium dissolves readily in liquid chlorine, it is not surprising that a solution of chlorine in liquid phosgene attacks aluminium so energetically that, unless the heat resulting from the reaction is withdrawn, the tube explodes violently.

The great chemical activity of aluminium chloride as displayed in a great variety of ways in both organic and inorganic chemistry, suggested that the solution of it in phosgene might have unusual properties. The first experiment carried out in this direction showed that this was actually the case, and opened up a wide field for investigation.

Metallic potassium, exposed to the action of a solution of aluminium chloride in phosgene, immediately began to react; a gas was formed, and the metal was slowly corroded, forming an insoluble compound, which, in the light of another investigation carried out in this laboratory, appears to be the phosgenate of a slightly soluble double salt of potassium chloride with aluminium chloride[3].

I had hoped, before making the trial, that it might be possible to displace aluminium from the chloride by a metathetic reaction with potassium, since the reaction would be exothermic:

$$3K+AlCl_3 \longrightarrow 3KCl+Al+154 \text{ Cal.}$$

The heat of solution of aluminium chloride in phosgene has not been determined, but the thermal effect is not great. The fact that potassium chloride is insoluble seemed to give the reaction formulated above plausibility. That metathetic reactions of this type may take place in non-aqueous solvents has been shown, for example, by Kraus[4] and by Bergstrom[5]. It is true that ammonia resembles water in that it forms conducting solutions, while phosgene probably does not; but Kahlenberg[6] found that zinc displaces hydrogen from a perfectly dry solution of hydrogen chloride in benzene, which conducts no better than pure benzene, he says. I can find no record of the dielectric constant of phosgene. Using Thwing's formula which connects the dielectric constant with the chemical constitution[7]

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[1] Bull. 27, 288 (1920).

[2] Gautier and Charpy: Compt. rend., 113, 597 (1891); Beckmann: Z. anorg. Chem., 51, 99 (1906). Cowper: J. Chem. Soc., 43, 153 (1883).

[3] Germann and Gagos: Science, 58, 309 (1923).

[4] J. Am. Chem. Soc., 44, 1224 (1922).

[5] Ibid., 45, 2788 (1923).

[6] J. Phys. Chem., 6, 5 (1902).

[7] Thwing: Z. physik. Chem., 14, 286 (1894).

$$K=\frac{D}{M}(a_1K_1+a_2K_2+a_3K_3 \quad \ldots .)$$

where D is the density of the substance, M its molecular weight, K_1, K_2, K_3 etc., specific constants depending on the element or atomic group involved, and a_1, a_2, a_3 the number of each occurring in the formula, the calculated dielectric constant varies according to whether we look at phosgene as a characteristic carbonyl compound, which gives a value of the same order of magnitude as the experimental value for acetyl chloride, or as a simple carbon compound, which would place it in the class with benzene. In the first case, the value is 24.1 at 15°, in the second case 3.6. There is no reason why the whole question should not be settled experimentally.

Conclusion

A review of the reactions of phosgene in the inorganic field indicates that phosgene is particularly reactive at temperatures where it is appreciably dissociated into chlorine and carbon monoxide. At lower temperatures phosgene reacts readily in many cases, especially where the reacting substance or a product of the reaction is soluble. Metals react more or less readily in the presence of aluminium chloride, depending on the solubility of the double salt of the chloride of the metal with aluminium chloride. Light does not decompose phosgene in glass containers, but it may act catalytically in promoting certain reactions with phosgene.

This work was carried out in collaboration with the Chemical Warfare Service, with phosgene supplied from the Edgewood Arsenal.

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THE FREEZING POINT CURVE OF THE SYSTEM WATER-AMMONIA

BY LOUIS D. ELLIOTT

The existence of two crystalline hydrates of ammonia is indicated by the work of Pickering,[1] Smits and Postma,[2] Rupert,[3] and Postma,[4] upon the freezing point curve of the system water-ammonia. Postma, agreeing closely with the work of Rupert, found the hydrate $2NH_3.H_2O$ to crystallize in very small needles melting at −78.9° while the other hydrate, $NH_3.H_2O$, was found to form much larger needles melting at −79.2°. From the form of their curves the hydrates are apparently largely dissociated in solution. Friedrichs[5] has recently questioned the existence of these hydrates suggesting that it may be a case of mixed crystals in continuous series.

In connection with the writer's investigation of the molecular lowering of the freezing point of liquid ammonia[6] it was thought worth while to continue the study of the solute water over as large a portion of the freezing point curve of the system water-ammonia as the adaptability of the apparatus would permit. Although the apparatus was not designed for this type of investigation the procedure was such as to render possible a careful study of the formation and appearance of crystals along the curve. Accordingly water was added to the freezing cell in increasing quantities and observations taken in the same manner as in the work upon the molecular lowering. After taking the freezing point temperature a lamp was held behind the cell so that the crystals could be critically examined. The freezing points obtained are tabulated below.

Mol.% NH_3	Obs.F.P.	Mol.% NH_3	Obs.F.P.	Mol.% NH_3	Obs.F.P.
100.0	−77.73°	80.6	−92.10°	64.3	−79.39°
99.4	−78.11	80.1	−94.33	61.0	−83.12
98.5	−78.58	80.0	−90.56	60.0	−85.03
97.3	−79.34	79.7	−90.20	58.8	−85.47
94.5	−81.01	79.1	−88.80	57.9	−87.25
91.0	−83.45	77.7	−86.98	57.3	−88.39
89.9	−84.13	76.4	−85.54	55.8	−84.54
86.6	−87.05	75.0	−83.56	53.3	−80.93
84.6	−89.37	74.2	−82.05	50.8	−79.12
83.5	−90.07	70.4	−80.03	47.8	−80.15
81.8	−91.86	68.6	−79.10	37.0	−97.0
80.9	−92.83	66.2	−78.88		

Eleven of the first thirteen readings are those determined in connection with the previous investigation upon the freezing point constant. For the determination of the freezing points of the solutions containing more than twenty five percent water the filling pipette previously used and described was replaced by one containing 26.0 grams of ammonia.

The results are shown graphically in the accompanying chart in which our results are plotted together with those of Postma for comparison.

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[1] J. Chem. Soc., 63, 141 (1893).

[2] Z. anorg. Chem., 71, 250 (1911).

[3] J. Am. Chem. Soc., 31, 866 (1909); 32, 748 (1910).

[4] Rec. trav. chim., 39, 515 (1920).

[5] Z. anorg. Chem., 127, 228 (1923).

[6] Elliott: J. Phys. Chem. 28.

Ammonia crystals which separated out until the first eutectic was reached were flock-like in character without any distinguishable crystalline form. The crystals of $H_2O.NH_3$ separating between the first and second eutectic were very distinct, comparatively large needles. There was no indication of the formation of mixed crystals at any time. The increasing viscosity noticed by previous investigators began to evince itself in the neighborhood of about 60% ammonia. Hand stirring was resorted to at this point. Supercooling became much more marked, soon amounting to about ten degrees. Crystallization under those conditions being quite sudden caused the formation of such a large mass of crystals that their form could not be determined with surety.

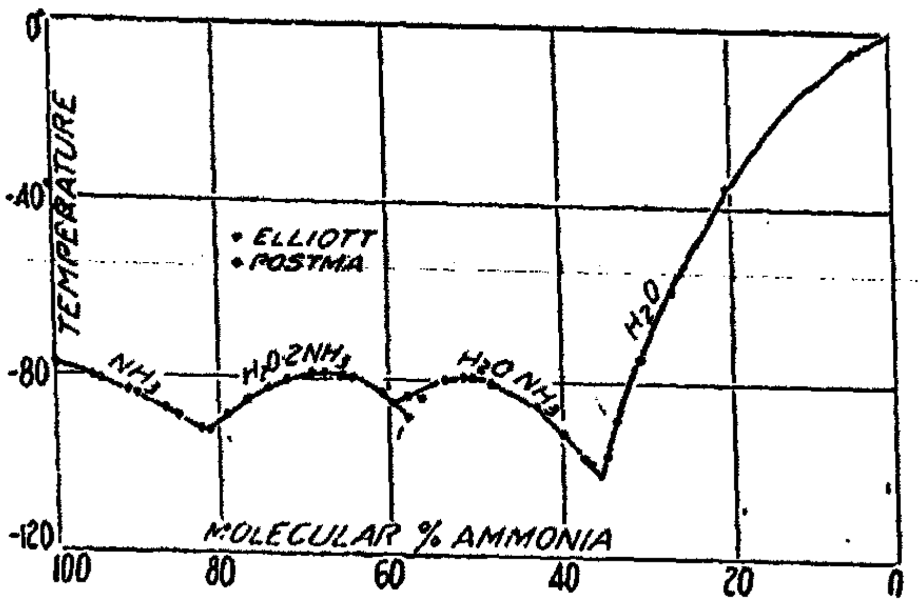

FIG. 1
Freezing Point Curve of the System Water-Ammonia

In the last measurement recorded the viscosity was so great as to render efficient stirring impossible, the liquid resembling a semi-liquid glass. However, in each case a definite crystallization took place with the usual rise in temperature to a maximum in the course of a few minutes. Friedrichs[1] notes that in his work with these viscous solutions equilibrium failed to become established even after several hours. It was found in our investigation that a differential of about twenty-five degrees between solution and cooling bath was necessary to bring about crystallization and subsequent rise to the maximum with such viscous solutions at the low temperatures encountered in this region.

Though not definitely determined, earlier investigators calculated the freezing point of the eutectic between $NH_3.H_2O$ and H_2O to be in the neighborhood of −120° while Postma's measurements place it at about −100.3°. Owing to the great viscosity encountered at this concentration no further measurements were attempted in the present investigation. The position on the curve of our last value of −97.0° seems to indicate that Postma's eutectic of −100.3° is much more nearly correct than the lower value.

The eutectic between NH_3 and $2NH_3.H_2O$ was determined experimentally. After taking the reading of the freezing point of the needle crystals formed with 80.6 molecular percent ammonia the temperature was observed to fall until typical flocks of ammonia crystals also began to appear. After a slight supercooling and subsequent rise the temperature remained constant at −92.59°. This figure is in close agreement with Postma's corresponding figure of −92.5°. As a whole the results corroborate those of Postma and of Rupert in showing the existence of two crystalline hydrates of ammonia.

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[1] Loc. cit.

DIELECTRIC CONSTANT OF GERMANIUM TETRACHLORIDE

BY MARY E. LEAR

The germanium tetrachloride used for measuring its dielectric constant was prepared from germanium dioxide. About eight grams of the oxide was reduced to the black powder form of germanium by a stream of hydrogen gas, washed and dried. A silica tube and silica boats were used to withstand the temperature necessary for reduction. During the reduction, a slight black mirror formed in the cool portion of the tube.

The metallic germanium left in the boats was treated with chlorine gas from a cylinder of liquid chlorine, after purified nitrogen gas had been passed through to remove all air from the apparatus. The reaction was quite evident from the light appearing over the boats and a mild glow of the metal. The germanium tetrachloride condensed in the first of a series of U-tubes immersed in an ice-salt mixture. Nitrogen gas was passed through the apparatus at the end of the experiment to sweep out the excess chlorine. A yield of about ten cubic centimeters was obtained from five grams of germanium. The method followed was in general that of Dennis and Hance[1].

The product was then distilled and its boiling point measured. Using a thermometer, graduated in tenths of degrees, the boiling point read 84.40 degrees at a pressure of 735 mm. When corrected for pressure by Young's modulus[2] and for emergent stem by the method of Rimbach[3] using the table of Austin and Thwing[4], the above reading becomes 86.30 degrees.

For measuring the dielectric constant of the liquid, the apparatus of Drude as modified by Schmidt[5] was set up. Three condenser bulbs of varying capacities contained the liquids used in measurement. They were standardized with benzene, thiophene free, and acetone distilled over calcium chloride. The readings for the bulbs filled with air and with benzene gave two values of dielectric constants below that of germanium chloride and mixture of benzene and acetone, according to Drude[6], gave three values above that of the chloride. Not less than five scale readings were made for each liquid. On plotting the scale readings against the dielectric constants, curves were obtained, from which the dielectric constant of germanium tetrachloride was determined directly.

Results

Cell 1.	Dielectric	constant	at 30	degrees	. . . 2.60
Cell 2.	”	”	” 30	”	. . . 2.60
Cell 3.	”	”	” 30	”	. . . 2.75

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[1] J. Am. Chem. Soc. 44, 304 (1922).

[2] Young: "Fractional Distillation," 12, 14 (1903).

[3] Z. Instrumentenk. 10, 153 (1890).

[4] Austin and Thwing: "Physical Measurements," 156 (1895).

[5] Schmidt: Ann. Physik. 9, 919 (1902)

[6] Drude: Ann. Physik. 8, 336 (1902).

The average value for the dielectric constant of germanium tetrachloride is 2.65 at 30 degrees Centigrade. Thus the dielectric constant for this compound lies between the values found for the tetrachlorides of silicon and tin, as predicted by Dr. Schlundt in his determinations of dielectric constants of inorganic solvents.[1]

Silicon tetrachloride D. C. at 17 degrees	2.18
Germanium tetrachloride D. C. at 30 degrees . .	2.65
Stannic chloride D. C. at 22 degrees	3.2

Germanium tetrachloride, having a low dielectric constant, would be expected to follow the Nernst-Thomson rule and possess no ionizing power.[2]

I wish to express my appreciation for the direction and assistance of Dr. Schlundt, under whose supervision the measurement was made.

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[1] J. Phys. Chem. 8, 130 (1904).
[2] Z. physik. Chem. 13, 531 (1894).

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SODIUM ALIZARATE AND ALUMINA

BY F. S. WILLIAMSON

It has been suggested by Liechti[1] that when hydrous aluminum oxide and sodium or ammonium alizarate are brought together, a true aluminum alizarate is formed. It is known that when hydrous chromic oxide or hydrous ferric oxide[2] is mixed with sodium alizarate no true compound is formed, but that it is a case of adsorption. Due to the similarity between these substances and hydrous alumina, it seemed probable that an adsorption complex of hydrous aluminum oxide and sodium alizarate would result when hydrous alumina is mixed with sodium alizarate and not a definite compound, aluminum alizarate.

The following experiments were conducted in order to establish the fact that the compound "aluminum alizarate" does not exist. If sodium alizarate reacts with hydrous aluminum oxide to form an aluminum alizarate, sodium hydroxide must be set free by the reaction. If it is a case of adsorption, the sodium alizarate will be taken up unchanged and there will be no sodium hydroxide found in the solution.

The first experiment was performed to settle this point. A solution of aluminum acetate was prepared and the alumina precipitated from this solution by the addition of ammonium hydroxide. The precipitate was allowed to settle and was washed thoroughly by decantation with distilled water. The alumina suspension was then analyzed and found to contain 0.5708 gram of Al_2O_3 per 25 cc. A sodium alizarate solution was then made up containing 2.84 grams per liter.

Twenty-five cc of the alumina suspension were placed in each of five 150 cc glass stoppered bottles. To each of these five portions was added a definite amount of sodium alizarate. The volume of the mixture in each bottle was made up to 50 cc and the bottles shaken in an automatic shaker for ten hours. The bottles were then removed from the shaker, the contents allowed to settle, and the supernatant liquid tested for sodium hydroxide. The quantities of sodium alizarate used were so chosen that practically complete adsorption of the dye by the alumina occurred even at the highest concentration. The shaking was done at room temperature.

No.	cc. Alumina	cc Sodium Alizarate	grs. Sodium Alizarate
1	25	5	0.0142
2	25	10	0.0284
3	25	15	c.0426
4	25	20	0.0568
5	25	25	0.0710

The tests showed that the supernatant liquid from each of the bottles contained no sodium hydroxide. The liquid gave no color with phenolphthalein and a neutral color with methyl orange, and required but one drop of N/10

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[1] J. Soc. Chem. Ind. 4, 587 (1885); 5, 523 (1886).

[2] Bull and Adams: J. Phys. Chem. 25, 660 (1921).

HCl to turn it acid. This proves that no sodium hydroxide is set free when sodium alizarate is adsorbed by alumina, but that it is taken up unchanged. This would indicate that it is a case of adsorption and that a definite compound is not formed.

The effect of acid upon the lake produced in the first experiment was now studied. To bottle number two, from the preceding experiment, small portions of N/20 acetic acid were added, the bottle and its contents being thoroughly shaken after each addition. A similar procedure was carried out with bottle number four using N/10 hydrochloric acid. It was found that the addition of more than sufficient acid to react with the sodium alizarate present had no effect upon the lake formed. After a time some peptization occurred, but the color of the lake remained unchanged. When the hydrochloric acid was added before the sodium alizarate, no different result was obtained.

However, when strong acid was added to the lake, the color was changed, varying from yellow to brown, depending upon the amount of acid used. This is probably due to the decomposition of the sodium alizarate by the acid with the formation of yellow alizarine.

The action of aluminum chloride upon ammonium alizarate was next tried out. It was found that upon mixing aluminum chloride and ammonium alizarate alone very little of the aluminum chloride hydrolyzed to form aluminum hydroxide. To overcome this difficulty enough sodium hydroxide was added to react with all the aluminum chloride present, thus assuring the formation of enough aluminum hydroxide. Several mixtures were made up in which the amounts of Al_2Cl_6 and sodium hydroxide were kept constant and the amounts of ammonium alizarate steadily decreased. These mixtures were boiled for three hours using a return condenser. At the end of this time the precipitate was allowed to settle and the supernatant liquid decanted off. The precipitate was washed once by decantation and then dried carefully over a low flame.

The colors of the various precipitates obtained were compared and the colors of the liquid portions as well. It was found that as the amount of ammonium alizarate in the mixture was cut down, the color of both the precipitate and the supernatant liquid became lighter.

The results of this experiment seem to prove that when sodium or ammonium alizarate is taken up by alumina, a definite compound is not formed but that the alumina adsorbs more alizarate as the amount of alizarate in the original mixture is increased.

Summary

Experimental evidence has been produced to show that an adsorption complex results when hydrous aluminum oxide and sodium or ammonium alizarate are mixed together, and that no definite aluminum alizarate is formed under these circumstances.

Cornell University.

NEW BOOKS

Metallographie in Elementarer Darstellung. *By Rudolf Ruer. Second edition. 23×16 cm; pp. x+347. Leipzig: Leopold Voss, 1922. Price: 10 shillings.* Some eighteen years ago Professor Gustav Tammann, Director of the Institute of Physical Chemistry in Göttingen, turned his attention to the study of metallic alloys. With the aid of numerous students he made a rapid survey of the constitutional diagrams of binary metallic systems. The methods used were comparatively rough but they were no doubt suitable for a preliminary survey of equilibria in metallic systems such as he had in mind. Two methods were principally used (1) thermal analysis and (2) microscopic investigation. By these means, the broad features of the diagrams were determined with fair accuracy but the methods, particularly those of thermal analysis, were not sufficiently sensitive for determining small heat changes. Accordingly, much of the work had to be repeated and has resulted in considerable modifications of and additions to these early diagrams.

In the interval, metallography has made great strides. To-day it rests on three great sciences, chemistry, physics, and crystallography. So far as its chemical aspect is concerned, it may be regarded as a branch of inorganic chemistry. It has a very close relation with several branches of physics. It is intimately bound up with crystallography since the properties of metals, whatever their condition may be, are the properties of the crystals of which they are composed. Moreover, during the last few years, the work of Laue, Hull, the two Braggs, Vegard, Debye, and Scherrer in the field of X-ray methods of investigation has opened up fresh avenues of investigation in this field. Tammann's "Lehrbuch der Metallographie" takes full cognizance of these developments and is a most interesting and valuable work. Professor Tammann is an independent thinker and his book is chiefly an expression of his own views. It is, in many respects, unlike any other book dealing with the same subject. Most books deal at considerable length with the technique of microscopic metallography, the preparation of metal sections and their microscopic investigation, the taking of heating and cooling curves, the construction of equilibrium diagrams, and a discussion of many of their features in detail. The author has broken away from this practice and has considered metallography from the standpoint of single, binary, ternary, and more complicated equilibrium systems.

Pages 1 to 169 deal with various aspects of "Einstoffsysteme" e.g. (1) the process of crystallisation in its broadest aspects, (2) the change of properties produced by changes of state and (3) the influence of mechanical work on properties.This last constitutes one of the newest and most important chapters of the book and will probably be found very interesting by English readers. In this country the work of Beilby on the hard and soft states of metals has profoundly influenced scientific opinion as to the changes in structure which correspond to the changes of properties observed. Beilby's view, however, that layers of amorphous material are produced at surfaces of slip by mechanical deformation has never been accepted by Tammann, who claims that there is no need for such a hypothesis, that the facts are inconsistent with it, and that they can be explained without supposing any destruction of the crystalline material to occur. Whatever may be thought of his handling of this subject, it should certainly be carefully studied, even though it may give English readers the impression that it does not sufficiently take into account the large number of facts brought within the purview of Beilby's theory. The high degree of symmetry possessed by most metals—the majority of them crystallise in the regular system—is commented upon by Tammann who points out that nearly all the technically important metals possess the same crystal lattice, viz. the face-centred cube. Iron at the ordinary temperature is an important exception to this since below 900°C it has a body-centred cubic lattice. Only between 900° and 1400°C has it the face-centred cubic lattice structure.

Binary systems occupy by far the greater part of the remainder of the book. Here again Professor Tammann's treatment is his own. We notice that, in giving his account of that most important of diagrams, the iron-carbon equilibrium, he adheres to the hypothesis of a double diagram, viz. the iron-graphite system (stable) and the iron-cementite system (metastable). On the whole, although there is still something to be said for this, the trend of opinion is decidedly against it. The great majority, if not all, of the facts can be explained on the single diagram, iron-cementite. There is no evidence that from pure iron carbon alloys graphite ever separates from the melt. Where its formation is observed it can be explained as being due to decomposition of the cementite which crystallises first. As Honda and Murakami have shown with some degree of probabiltiy decomposition of cementite takes place very easily in the presence of oxides of carbon. If pains are taken to ensure their absence the carbide appears to be much more stable. We gather that Tammann regards the β to α change in iron as a phase change. This also is against the general trend of scientific opinion. The change of properties is most probably due to the rapid increase in ferro-magnetism at this temperature and this is not a phase change. X-ray analysis has confirmed the view already held that between β and α iron no difference in crystal structure exists. The iron nickel diagram given on page 290 does not represent by any means the latest work on this equilibrium and should certainly be brought up to date. The copper-zinc equilibrium given on page 299 completely ignores the inversion at 470°C found in the β constituent by Carpenter and Edwards thirteen years ago.

A brief discussion of crystallisation and equilibria in ternary and quaternary systems and phase rule completes the volume.

H. C. H. Carpenter

Couleur et Constitution chimique. *By J. Martinet, with the collaboration of Mlle. P. Alexandre. Collection Langevin-Perrin-Urbain. pp. 324. Paris: O. Doin, 1924. Price: 25 francs.*

This latest work on the connection between colour and constitution is written from the point of view of the organic chemist and, as such, deserves the highest praise. The ultimate physical cause of selective absorption is referred to only briefly, the author holding the view that discussion of this question belongs more to the province of the physicist than of the chemist. "Reconnaître si un corps était coloré ou non, prévoir dans une certaine mesure la longueur d'onde des radiations absorbées par simple examen de la structure chimique, tel était notre but".

A short introduction deals with definitions, causes of colour and such matters as unsaturation and conjugated double linkages. The importance of the latter in the structure of coloured compounds is very noticeable when one turns to the following chapter on coloured hydrocarbons. Whether hydrocarbons could exhibit colour was a debatable point thirty years ago. Now, however, a large number are known and the author draws particular attention to the isomerism of the colourless xylenes and the orange dimethylfulvene. Not only does conjugation of double linkages play an important part in shifting absorption to the visible portion of the spectrum, but also ring building. This is very plainly shown in a comparison of colourless diphenylbutadiene with yellow benzylidene-indene and of slightly yellow diphenylhexatriene with red cinnamylidene-indene.

The method of arranging material for a work such as that under consideration, is not easy and the choice has been made to consider chromophores, auxochromes and their mutual relationships in Chapters II, III and IV respectively. This division of subject matter may appear somewhat antiquated but this cannot be said of the way in which the material is handled; moreover, one is continually reminded of the almost constant association of colour with conjugated double linkages.

In dealing with salt formation and colour change, meriquinonoid compounds, organo-metallic complex formation, chromoisomerism, thermotropism and phototropism, accounts are given which well represent the views of the authors with whose names these subjects are usually associated. In fact, the references to literature throughout the work testify to the extraordinary pains taken in collecting data respecting the constitution of coloured compounds.

At the same time, English chemical literature has not been as thoroughly ransacked as it might have been. One misses the work of A. G. Green and A. G. Perkin on the phthaleins, and G. T. Morgan is not mentioned in connection with coloured organo-metallic complexes.

The method of calculating the position of absorption bands due to J. Moir and the work of J. E. Purvis on the spectra of vapours of organic compounds have also escaped notice.

The chapters on chromophores and auxochromes in relation to physical and chemical properties as well as the conclusion are full of interest.

The book finishes with a table of contents; it is unfortunate that there is no index. Despite this shortcoming, the work is to be heartily recommended as giving an up-to-date account of the relationship between constitution and colour in a clear, readable and impartial manner.

J. T. Hewitt

Practical Physical Chemistry. *By Alexander Findlay. Fourth edition. 22×16 cm: pp. xvi+298. New York and London: Longmans, Green and Co., 1923. Price: $2.25.* "Sections have been added which deal with the new ebullioscopic method introduced by Cottrell, with the Abbe refractometer, and with the Hilger wave-length spectrometer (constant deviation type). In the chapter on electromotive force, also, I have inserted sections dealing with oxidation and reduction potentials, and with the methods of electrometric analysis, including the determination of hydrogen ion concentrations which are coming increasingly into use and ought to be more widely known. In view, also of the importance of colloids in pure as well as in applied science, a chapter dealing with some of the more important properties associated with the colloidal state has been added. An exhaustive treatment of the very wide and important field of colloid chemistry could not, of course, be attempted here, but it is hoped that the experiments described will serve as a suitable introduction to practical work in colloid chemistry, or will, in any case, have the effect of directing the students' attention to this branch of chemistry."

The chapter on colloids includes: the preparation of colloidal ferric hydroxide and arsenious sulphide sols; cataphoresis; mutual precipitation of colloids; precipitation of suspensoid colloids by electrolytes; protective action of emulsoids; adsorption; the adsorption isotherm.

Wilder D. Bancroft

Die Methoden der organischen Chemie. *By J. Houben. Vol. II. Second edition. 28×18 cm; pp. xxvii+1115. Leipzig: Georg Thieme, 1922. Price: Paper, $7.20, bound, $8.00.* The subject matter is presented under the headings: oxidation and reduction by R. Stoermer; catalysis by H. Meerwein; condensation by R. Kempf; double and triple bonds by R. Stoermer; preparation and use of the most important enzymes by J. Meisenheimer; decomposition of optically inactive substances into their active components by H. Scheibler; electrochemical methods by K. Arndt; electro-osmotic methods by P. H. Prausnitz; reactions under high pressure by K. H. Meyer; photochemistry by J. Houben.

The book contains a wealth of information and nobody could fail to find in it much that was both new and interesting to him. A few of the points that happened to appeal to the reviewer are: the oxidation of toluene to benzoic acid with chromyl chloride, p. 6; the formation of peracetic acid, p. 29; the oxidation of glucose with hypo-iodite, p. 33; Fenton's oxidations with hydrogen peroxide and ferrous sulphate; the behavior of gum arabic as a protecting colloid, 271; aluminum amalgam as a substitute for the Gladstone and Tribe zinc-copper couple, p. 295; nascent hydrogen from formic acid, p. 418; the effect of manganese salts on the oxidation of aldehyde, p. 422; the oxidation of glucose in presence of cerium hydroxide, p. 423; silver peroxynitrate as a carrier, p. 425; the action of piperidin on tautomeric forms, p. 473; induced reactions, p. 917; the tungsten mercury lamp, p. 929; the ionization of anthracene by light, p. 957; the action of blue light on hydriodic acid, p. 964; the conversion of acetone to methane or ethane, p. 970; the polymerization of acetylene, p. 1023; the production of indigo from indican, p. 1040.

One could extend this list indefinitely but these instances will suffice to show the extraordinary value of the book for reference purposes. The tabular statements of the properties of oxidizing agents, etc. on pp. 177, 373, 737, will be found extremely helpful. It is a pleasure to note that there will be at least two more volumes.

Wilder D. Bancroft

Lehrbuch der Physik. *By Bernhard Dessau. Vol. I. 24×17 cm. viii+667. Leipzig: Johann A. Barth, 1922.* This first volume deals with mechanics, acoustics, and heat. The book is intended to come between the short text-books and the bulky hand-books. The purpose is to give a scientific presentation in such a form that it will call attention to the unsolved problems and thus to stimulate the reader to do his own thinking and to study the original literature. The reviewer got this statement out of the preface and it seems not to have gone any farther.

There are a number of places where the author is dealing with problems of physical and colloid chemistry and, as is only natural, those are obviously the weak spots. No one would ever guess, p. 279, that all the careful measurements had shown the non-existence of a contact angle when a liquid wets a solid. A semipermeable membrane, p. 292, is distinctly not necessarily a limiting case of an ultra-filtration membrane with very small pores. It seems like going pretty far back to give de Saussure's data on the adsorption of gases by charcoal, p. 342. In view of what we know about the squirting metals, it does not seem certain that the flow of a glacier, p. 542, is entirely a question of ice melting under pressure. Under dilute solutions, p. 600, the author deduces the Raoult formula and not the van't Hoff formula. There is also no suggestion as to such sources of error as the volume occupied by the solute or the heat of dilution. The phase rule is given four pages of fine print; but the author makes the extraordinary statement, p. 606, that at each temperature an absolutely definite percentage of calcium carbonate decomposes into lime and carbon dioxide. The reviewer had supposed that the amount of decomposition varied with the ratio of the vapor phase to the solid phases. It is the pressure and not the percentage decomposition which has a single value for each temperature.

Wilder D. Bancroft

Lehrbuch der Metallographie. *By Gustav Tammann. Third edition. 25x16 cm; pp. xviii+450. Leipzig: Leopold Voss, 1923. Price: 14 shillings, six pence.* This volume is by Dr. Rudolph Ruer, a pupil of Professor Tammann. The first edition of his book appeared in 1907. The present edition (the second) was published in 1922. The scope of the work is altogether much more restricted than that by Professor Tammann.. Almost the whole of the book is concerned with equilibria in binary metallic systems. The author has founded his treatment on the classification of equilibria in heterogeneous systems introduced by Roozeboom. The general treatment of this subject occupies nearly 200 pages and is on perfectly orthodox lines. The author then considers a number of typical binary systems including of course that of iron-carbon. In this he follows Tammann in adopting the hypothesis of a stable and meta-stable system of equilibrium. What has been already said above applies therefore equally to Professor Ruer's treatment of this subject. He has a section entitled "Experimenteller Nachweis der Existenz zweier verschiedener Eisen—Kohlenstoffsysteme", but we have not found this in any way convincing. He gives 1152°C as the equilibrium temperature for the austenite-graphite eutectic and 1145°C for the austenite-cementite eutectic. Whether these are real differences or whether they are due to supercooling effects cannot be definitely said. At all events the former hypothesis cannot be regarded as established. Professor Ruer gives in conclusion a very brief treatment of three-component systems and practical aspects of the thermal and microscopical investigations of alloys.

H. C. H. Carpenter

1-1238

THIRD REPORT OF THE COMMITTEE ON CONTACT CATALYSIS[1]

BY HUGH S. TAYLOR

The following report aims to present a summary of recent investigations which seem to advance our understanding of the nature of contact catalysis, its mechanism and general technique. It is not an exhaustive summary of the catalytic researches carried out in the preceding year. The grouping of the researches has been made with regard to their bearing on specific points of interest which it is desired to emphasize, not necessarily on a similarity of reaction.

Wall Reactions

The scope of the subject under investigation is extending continuously. Considerable attention is now being paid, not only to catalysts deliberately inserted into a reaction system, but also to the acceleration of reactions by the walls of the containing vessel. The work of Hinshelwood, Hartley, and co-workers, mentioned in the previous report with respect to the decomposition of formic acid on glass surfaces and on silver and platinum has been extended to include different glasses and other metals. The type of reaction has been varied to include other typical decompositions of gases including hydrogen peroxide, chlorine monoxide, sulphuryl chloride, and phosphine.

One outstanding conclusion from this work is to emphasise anew that true unimolecular reactions are, as yet, conspicuous by their absence. All of the known cases which have been presupposed unimolecular, have proved to be either wall reactions or reactions occurring on collision. It is therefore evident that we do not yet need, for any known reaction, the concept of radiation to give an explanation of the occurrence of unimolecular reactions.

Bimolecular reactions between gases, likewise, are being shown to be wall reactions. The two notable cases investigated recently are the combination of ethylene and bromine and the combination of nitric oxide and oxygen, reactions hitherto generally regarded as gaseous reactions, now shown to be tremendously sensitive to the nature of the vessel in which they are contained. It must also be borne in mind that, even when wall effects are demonstrably small, the gas reaction may still be a catalysed reaction. The effect of water vapour on the combination of hydrogen and oxygen, and of carbon monoxide and oxygen shows that these reactions are not simple collision reactions but that water is a contact catalyst, molecularly dispersed, or, if you will, forms intermediate compounds. The insensitivity of dried gases to reaction seems to demonstrate that it is not the energy of collision which brings about inter-

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[1] Report of the Committee on Contact Catalysis of the Division of Chemistry and Chemical Technology of the National Research Council. Written by Hugh S. Taylor, assisted by the other members of the Committee: Messrs. H. Adkins, W. C. Bray, O. W. Brown, R. F. Chambers, C. G. Fink, J. C. Frazer, E. E. Reid, and W. D. Bancroft, Chairman.

action, since small quantities of water vapor cannot alter this magnitude. The water vapor molecules, highly polar, must behave in the same manner as do contact catalysts in activating the several molecular species. This point has been raised in a slightly different form by Hinshelwood. It is also discussed by Norrish in some extracts given below.

Hinshelwood and Prichard[1] have studied the thermal decomposition of hydrogen peroxide, and of sulphuryl chloride in the gaseous state, and the thermal decomposition of chlorine monoxide. Diazoacetic ester was also examined, but found to be unsuitable for quantitative measurements, as tarry deposits were formed. The decomposition of chlorine monoxide proved to be homogeneous, whilst the hydrogen peroxide reaction and the sulphuryl chloride reaction were found to be typical heterogeneous reactions.

Concerning such heterogeneous reactions the authors write: "When a molecule is adsorbed by a surface, the forces between it and the molecules constituting the surface modify the internal forces in a way which is at present quite incalculable and must be entirely specific. Generally speaking, it must be expected that the stability would be increased as often as it is decreased. Yet, the accumulation of observations showing that almost any gas reaction takes place more readily on a given surface such as glass than in the homogeneous phase, raises the question whether the operation of some general cause is not superimposed on the various specific influences. In the case of combinations in which two or more molecules are involved, the encounter of two types is obviously facilitated by the more or less prolonged sojourn of one of them on the surface, but this factor is inoperative in the case of the simple unimolecular decompositions. It seems relevant, therefore, to ask whether one universal factor may not be simply the second law of motion. Consider a molecule composed of two parts, A and B, the disruption of which constitutes the decomposition of the molecule. Let B receive an impact from another molecule which imparts to it momentum directed away from A. The small inertia of A, however, enables it to follow B, without the development of much strain between the two. If, however, A were firmly enough held to a surface, its inertia might be so great that the accelerating force, instead of drawing A after B, would cause the disruption of the "bond" between them. The reluctance of homogeneous gas reactions to proceed might thus be due to the small inertia of the different parts of the molecules rendering disruption by collision very improbable. This is only suggested as one of several possibilities. That it is a mechanical picture, whilst we now believe "activation" to consist in the passage of an electron to an orbit of higher quantum number, is not a relevant criticism, since the results of work on the collision of electrons with gas molecules show that a definite correlation exists between quasi-mechanical and quantum processes.

"The thermal decomposition of chlorine monoxide proved to be a homogeneous reaction uninfluenced by the glass walls of the containing vessel. The velocity of reaction increases as the change proceeds. This is not due to autocatalysis, since oxygen and chlorine have no influence on the rate of

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[1] J. Chem. Soc., 123, 2725, 2730 (1923).

decomposition, but is attributed to the occurrence of the change in consecutive stages. The rate of reaction at 131.3° is inversely proportional to the initial pressure of the chlorine monoxide, and the influence of pressure appears to operate uniformly throughout the course of the change at this temperature. Hence the decomposition depends on a collision effect and is not a spontaneous unimolecular process.

"The influence of temperature on the reaction is such that the time required for the change to proceed from 40 per cent, to 80 per cent. is increased 2.03 times for every 10° decrease in temperature between 131.3° and 110.7°. From the influence of temperature and from the heat of reaction it is shown that explosion waves should be readily propagated in the gas."

Norrish[1] seeks to formulate the Arrhenius concept of active and passive molecules in terms of catalytic activation by either homogeneous or heterogeneous catalysts. Among the former, water vapor is important in gas reactions. The walls of the containing vessel are included in the latter.

"Even the most reactive substances become inert upon complete desiccation, and will then regain completely their lost activity by the addition of a trace of some polar substance. In other words, all chemical reactions appear to be catalytic in nature. Except in the case of a few truly thermal decompositions of solids or liquids such as potassium chlorate, silver oxide, and lead acetate, the formation of ozone by the electric discharge, and possibly some unimolecular photochemical decompositions, this loss of reactivity on desiccation would appear to be a general rule of chemical reactivity, and, if accepted as such, it necessitates a revision of our views of activation; the resting form of a molecule must be a far more inert substance then hitherto supposed, and require the association of some polar molecule before activation can take place. When we remember that the main characteristic of a polar molecule is its strong unbalanced field of force, it appears very probable that its function as a catalyst is to weaken, by close association, the intramolecular forces of the resting molecule, and to render it more easily disintegrable.

"We may thus consider those molecules which have formed a close association with molecules of the catalyst to be, at any rate, partly activated, inasmuch as they alone are capable of any further chemical action. Whether this is the complete stage or only a preliminary stage of activation it is not proposed to consider here, but there would appear to be no difficulty in the explanation of all the phenomena of chemical reactivity by the kinetic theory coupled with this view of activation alone, and without recourse to other hypotheses, as, for example, the "radiation theory."

"The catalytic effect of traces of polar substances on gaseous reactions is only one manifestation of a much more general phenomenon, and it may be said, that whenever any strong, local, disturbing force can be applied to a molecule, so as to distort its stable configuration, that molecule becomes more vulnerable to attack. Thus, the very numerous class of reactions which take place in solution probably owe their existence to the action of the solvent, which exerts a weakening effect on the internal molecular forces of the solute,

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[1] J. Chem. Soc., 123, 3006 (1923).

that may result, in extreme cases, in complete ionisation. Again, the phenomena of surface catalysis, and surface reactions, are manifestations of the same nature, and owe their existence to the high electrical fields of force which must exist unbalanced at the surfaces of most solids and liquids, and result in the adsorption and weakening of the structure of the reactant molecules.

"We may thus regard molecular activation as occasioned by a definite change of configuration or distortion of the molecule, brought about by close association with some polar catalyst. Such a change of configuration must take place with the absorption of energy, and thus the activated molecules will be in a more highly energised state than the resting molecules.

"These views are in harmony with those developed by Lowry in his work on the electronic theory of valency. In a comparative study of the reactions of unsaturated organic compounds, he has drawn the conclusion that substances containing the double bond usually react as if one of the bonds were a covalence and the other an electrovalence. On this basis, the formation of ethylene dichloride from ethylene and chlorine involves an unsymmetrical instead of a symmetrical process of activation thus: $CH_2=CH_2$ and $Cl-Cl$ give $\overset{+}{C}H_2-\overset{-}{C}H_2$ and $\overset{+}{Cl}\ \overset{-}{Cl}$ as an intermediate stage, rather than $-CH_2-CH_2-$ and $2Cl-$. The chlorine is here represented as being broken into two ions instead of two neutral atoms, in the disruption which must precede or accompany its attachment to the ethylene. The unsymmetrical rupture or opening out of the double bond of the ethylene gives rise to an analogous process of intramolecular ionisation, since the two charged atoms are not free but bound. The final interaction between the two activated molecules is then reduced to a mere neutralisation of opposite ions. It differs from the union of $\overset{+}{Ag}$ with $\overset{-}{Cl}$ mainly in that the ions yield covalent bonds on neutralisation instead of undissociated ionic pairs. The analogy between the development of an electrovalence on the one hand and the process of activation on the other is so complete as to suggest that the two phenomena are identical.

"The view set forth above, that molecular activation is a catalytic process of a polar character, is susceptible of direct experimental testing in the case of the gaseous reaction of ethylene and bromine, which has been investigated by Stewart and Edlund.[1] These two authors have shown that (1) ethylene and bromine at 0°, when dry, do not react together in the gaseous phase, but only on the glass walls of the container, and (2) there is no indication of a preliminary gaseous reaction such as might be expected if a few of the ethylene and bromine molecules were already activated in the gaseous phase.

"So far, these experiments are completely in accord with the hypothesis that activation of the ethylene molecule is due to polarisation induced in the ethylene molecule by association with some polar catalyst; but they are also capable of being explained on a merely physical basis, for example, by adsorption of the two gases on the surface of the glass, without reference to the chemical character of that surface.

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[1] J. Am. Chem. Soc., 45, 1014 (1923).

"It is, however, evident that if dry ethylene and bromine could be enclosed in a vessel with completely non-polar walls, it might be possible, if the above hypothesis of polar activation is correct, to retard the reaction very greatly, or even to suppress it altogether, although it is by no means certain that in all cases such a suppression could be looked for.

"The results which are contained in the experimental section of the paper must be taken as strong confirmatory evidence in favor of this hypothesis. It, has, for instance, been found that on enclosing the dry gases by a vessel the interior of which is coated with stearic acid, the reaction proceeds even more quickly than when the glass walls are pare, whilst, when paraffin wax is substituted for stearic acid, the reaction bractically ceases to take place. Now the work of Hardy,[1] Harkins[2] and Langmuir[3] has led us to regard the former of these two substances as a particularly polar molecule, whilst the paraffins constitute probably the best approach to a completely non-polar substance. Thus, in spite of their great physical similarity, a stearic acid surface brings about the combination of bromine and ethylene, whilst a paraffin wax surface does not, and this difference in their behavior can only be attributed to difference of polarity in the surfaces of the two substances occasioned by the marked chemical differences between their molecules.

"The importance of the experimental results recorded in this paper is considered to lie in the fact that they provide evidence of a new character in favour of the theory that molecular activation is not only of a catalytic character, but consists in an induced polarisation of the reactant molecules by association with some polar catalyst, either in the gaseous, surface, or liquid phase. They also confirm Lowry's deduction that molecules of unsaturated compounds may exist both in a non-polar "resting form" and in a polar reactive form, and further show that the conversion of the former into the latter may be brought about by a polar catalyst. This phenomenon is probably purely electrical in character, consisting simply in the production of an electrovalence from a covalence by a displacement of one of the electrons constituting the double bond, under the action of the electrical field of the catalyst.

Rideal writes that "the rate of the ethylene-bromine reaction can be used to test the polarity of certain varnishes used in the industries and that the results obtained parallel the results of surface tension measurements." It is quite possible that phosphorus trichloride and chlorine would display little tendency to react if a suitable container for the two gases were found. In such a container it would then be possible to determine the density of phosphorus pentachloride without dissociation occurring. The classical example of a bimolecular gas reaction, the hydrogen-iodine combination studied by Bodenstein, cannot be entirely free from the suspicion of catalytic influences. Calculations which purport to express the velocity with which such a reaction occurs, in terms of collision frequencies and critical energy increments would

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[1] Fourth Brit. Asso. Rep. on Colloid Chemistry, 185, (1922); also Proc. Roy Soc. 86A, 610 (1922).

[2] J. Am. Chem. Soc., 39, 354, 541 (1917.)

[3] Met. Chem. Eng., 15, 468 (1916); J. Am. Chem. Soc., 39, 1848 (1917).

necessarily need revision in case such catalytic influences were found. That the critical energy increment which a reaction requires is determined largely by such catalytic influences is very evident from recent work on the photochemical combination of hydrogen and chlorine. Tramm[1] has shown that visible light will not cause the combination of hydrogen and chlorine when the gases are thoroughly dried. But, gaseous mixtures, insensitive to visible light, can be combined with the aid of the larger energy quanta available with ultra-violet light; Coehn and Jung[2] have shown that thoroughly dried hydrogen and chlorine will combine when exposed to light whose wave-lengths are less than 2540 Å.

Hinshelwood and Hartley[3] have continued their work on formic acid decomposition at glass surfaces. Duroglass gave a much higher percentage of carbon dioxide and hydrogen as compared with carbon monoxide and water, than the earlier glass used. Nevertheless it was shown that the temperature coefficient of the carbon dioxide reaction is again with Duroglass markedly higher than the carbon monoxide reaction. The authors calculate the respective "heats of activation"[4] as $E_{CO} = 12000$ cals., and $E_{CO_2} = 24500$ cals., as compared with 16000 and 28000 calories respectively in the earlier work. Carbon monoxide is shown to have no retarding influence on the progress of the reaction at glass surfaces. Water vapor apparently accelerates the carbon dioxide reaction. This may account in part for an observed increase of carbon dioxide percentage with progress of the reaction, a fact originally due to Berthelot. To the reviewer this action of water vapor seems to indicate that the glass surface contains centres of activity which promote either the carbon monoxide reaction or the carbon dioxide reaction, but not both.

Hinshelwood and Topley[5] have extended the measurements of Tingey and Hinshelwood on the temperature coefficient of formic acid decomposition. To glass, platinum and silver as catalysts, rhodium, gold and palladium for the carbon dioxide decomposition and titanium dioxide for the carbon monoxide decomposition have been added. In this latter case, which yields almost exclusively carbon monoxide, the value of E_{co} is 29500 cals., whereas, with glass, E_{co} is 12000-16000 cals. A low value for the energy of activation of formic acid to yield carbon monoxide and water is not an inherent property of the formic acid molecule, but is determined in part by the surface accelerating the change. This is further evidence of the composite nature of the temperature coefficient of heterogeneous reaction velocities as emphasized by Pease. (See later section).

For the carbon dioxide reaction the values of E_{co_2} vary between 22000 and 31000 for glass, gold, silver, platinum and rhodium. There is no relation between these values and that of surface activity, which increases in the given series from 0.05 to 500 in the order named, platinum being set equal to 100.

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[1] Z. physik. Chem., **105**, 356 (1923).

[2] Ber., **56**, 696 (1923).

[3] J. Chem. Soc., **123**, 1333 (1923).

[4] Calculated from the temperature coefficient of reaction velocity by means of the equation $d \log k/dt = E/RT^2$.

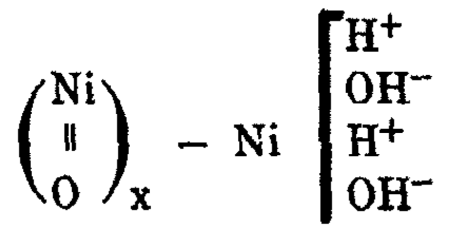
[5] J. Chem. Soc., **123**, 1014 (1923).

Palladium is abnormal showing wide variations in activity and temperature coefficient according as it is free from or contains occluded hydrogen. The latter decreases markedly the activity. Assuming the Langmuir monomolecular layer theory and no differences in 'phase' of the formic acid molecule or of modes of adsorption of the molecule, the authors calculated the fractions of the several surfaces covered at 200° and 2 atmospheres pressure. The fractions vary from 10^{-1} for silver and rhodium to 5×10^{-6} for glass. Evidence will be given later to show that this may represent that portion of the surface which is capable of catalysing the change under discussion.

Catalytic Hydrogenation

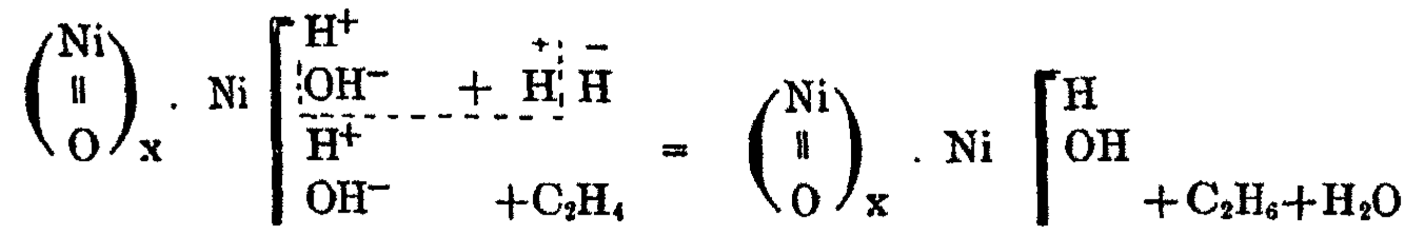
On the basis of experimental work by Cantels, Boswell[1] has sought to interpret the mechanism of catalytic hydrogenation by nickel, taking account of the role played by oxygen in such hydrogenations as first emphasized by Willstätter. The experimental data led Boswell to the following concept of the mechanism.

"Nickel oxide partially reduced at a low temperature consists of particles of nickel oxide surrounded by metallic nickel carrying positive hydrogens and negative hydroxyls alternately arranged on the surface in several layers; thus, with only one layer of hydrogen and hydroxyls represented—

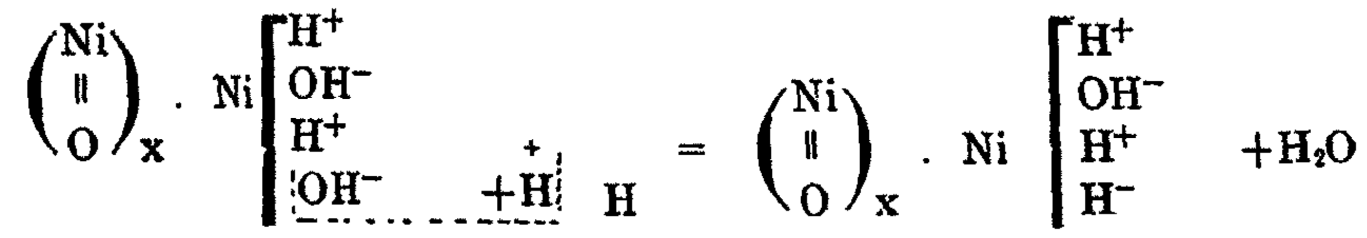


When this complex catalyses the union of hydrogen and ethylene four reactions occur:

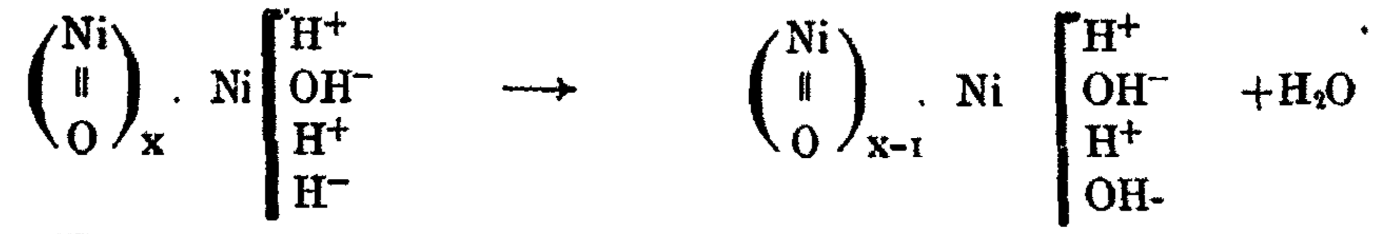
1 A very fast reaction



2 A very slow reaction



3 A very slow reaction



"Reaction (1) represents the main reaction which occurs. It expresses the mechanism of hydrogenation by an active nickel catalyser.

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[1] Proc. Roy. Soc., Canada, 16, Series III (1922).

"Reaction (2) represents the slow removal of negative hydroxyls from the surface of the catalyser and the adsorption of hydrogen constantly taking place.

"Reaction (3) represents the slow reaction of this adsorbed hydrogen with the unchanged nickel oxide in the interior of the particles.

"A fourth reaction also occurs, involving the addition of positive and negative hydrogens from neutral hydrogen molecules to the complex on the right hand side or reaction (1), to form the complex on the left hand side of reaction (3). This fourth reaction represents the mechanism of hydrogen adsorption.

"Equations (2) and (3) also represent the reactions which occur on continued reduction of nickel oxide by hydrogen. This continues until all the nickel oxide in the interior of the particles has been reduced and until finally all the hydroxyls on the surface have been removed and only adsorbed hydrogen, as positive hydrogens and negative hydrogens, remains. Thus the hydrogen which is taken up in excess of the equivalent of water formed is held on the surface in two ways: (1) as positive hydrogens and negative hydroxyls, and negative hydroxyls, and (2) as positive hydrogens and negative hydrogens.

"Evidently the water represented in these equations is not all evolved for if such were the case the catalyser would soon lose all its oxygen and, as will shortly be pointed out, lose almost entirely its capacity for catalysing hydrogenations. This water is only evolved in the free state in relatively small amount, the chief part remaining on the particles as hydrogens and hydroxyls. This is equivalent to saying that in reaction (1) a negative hydroxyl on the surface of the catalyser has a tendency to unite with a positive hydrogen of a neutral hydrogen molecule, thus loosening the bond between the positive and negative hydrogens of the hydrogen molecule sufficiently to permit the positive and negative hydrogens of the hydrogen molecule to unite with a molecule of ethylene. That is, the hydrogenation is pictured as occurring at the surface of the particles by means of oscillating hydrogen atoms which are at one instant more closely associated with the hydroxyls and hydrogens on the surface of the particles and at the next instant more closely associated with each other in hydrogen molecules. A small portion of the impacts of positive hydrogen of gas molecules and negative hydroxyls on the surface result in the permanent formation of molecules of water which are evolved as such.

"Reaction (2) represents a reaction very slow in comparison with reaction (1) and which is constantly taking place during the hydrogenation. Negative hydroxyls on the surface are constantly and very slowly being removed and hydrogen being adsorbed.

"Reaction (3) represents the reaction of this adsorbed hydrogen with unchanged nickel oxide in the interior of the particle. Here also the water represented is not all evolved in the free state but partly goes to reform hydrogen and hydroxyls on the surface.

"Finally, after long use the oxygen remaining on the catalyser either as negative hydroxyls or unchanged nickel oxide in the interior becomes very small and nothing remains finally but nickel particles with adsorbed hydrogen thus—

$$\mathrm{Ni}\left[\begin{matrix}\mathrm{H}^+\\ \mathrm{H}^-\\ \mathrm{H}^+\\ \mathrm{H}^-\end{matrix}\right.$$

Nickel in this condition is a very poor catalyst for hydrogenations. The activity of the catalyst is associated with its oxygen content and its activity can be restored by reoxidation and partial reduction.

"It follows from the experimental data that the absorption capacity of nickel for hydrogen depends on the method of preparation. If prepared from oxide by reduction with hydrogen at temperatures below 275°, it would probably require many months to remove completely all the oxygen. And as we have seen, the capacity of a nickel catalyst to hold hydrogen depends largely on its oxygen content. By continuous reduction at 275° for only ten hours, a condition is reached where the water evolved in half an hour is relatively very small. Should this be taken as an indication of the attainment of complete reduction an utterly erroneous result would be obtained for the hydrogen adsorption capacity of nickel, for the catalyst would still contain a large percentage of oxygen. This probably explains the widely varying statements in the literature regarding the amount of hydrogen which nickel can adsorb, varying from 0.2 vols. of hydrogen per volume of nickel to a capacity for hydrogen as great as that possessed by cocoanut charcoal.

"No meaning attaches to the measurement of hydrogen adsorption by nickel unless the whole history of the nickel is also described in detail. The term, it seems, should be restricted to the amount of hydrogen taken up by a known weight of nickel spread over a definite surface, the nickel having been prepared by the reduction of nickel oxide by hydrogen at a definite temperature until all the oxygen has been removed.

"As nickel oxide has an indefinite composition, being always a mixture of oxides, the completion of reduction by hydrogen cannot be determined by continuing the reduction until the water equivalent of the oxygen in the oxide has been evolved. There appear to be two ways of determining whether reduction has been complete or not: (1) to continue the reduction in hydrogen until no water is evolved, even after allowing the nickel to stand in the cold in an atmosphere of hydrogen for several hours and subsequently heating in a current of hydrogen; and (2) completely reduce at 400°C. and then oxidize with a known volume of oxygen at 400° and reduce at the desired temperature until the water equivalent of the oxygen adsorbed has been evolved.

"From the standpoint of catalysis of hydrogenation, however, the measurement of hydrogen adsorption is, as we have just seen, of little importance, as the normal nickel catalyst is never in the condition of holding hydrogen alone.

"Notwithstanding the relatively large amount of hydrogen adsorbed on a nickel catalyst prepared by partial reduction at 275°, ethylene alone, in the absence of free hydrogen, does not react at 150°C. For hydrogenation free hydrogen must also be present. This is also true for nickel prepared by complete reduction at 400°. That is, the hydrogens on the nickel catalyst in either of the two states, (1) positive hydrogens and negative hydroxyls and (2) positive hydrogens and negative hydrogens, do not react with ethylene at 150° in the absence of free hydrogen.

"According to the mechanism of hydrogenation by nickel just described, most of the conflicting views of investigators are, we believe, explained. The conception of definite hydrides as intermediate products in hydrogenating actions is not valid as the normal catalyst always contains oxygen and functions, as catalyst for hydrogenations, chiefly through the hydroxyl groups on the surface. Even where the catalyst carries only hydrogen this can not be said to exist in the form of definite compounds called hydrides of definite proportion of hydrogen to nickel, but rather as complexes in which nickel carries the hydrogen adsorbed on the surface as positive and negative hydrogens.

"Likewise the oxygen present in the normal catalyst is not there as a definite hydroxide of nickel, but as a complex carrying hydroxyl groups negatively charged along with hydrogens positively charged. However, although these combinations are "complexes" rather than compounds yet the hydrogens and hydroxyls react, it would appear, in stoichiometric proportions.

The recent researches of Kelber[1] must be considered as decisive however, in connexion with the question of the necessity of oxygen in nickel catalysts of high activity. Kelber has prepared nickel catalysts by reduction of nickel cyanide in hydrogen at various temperatures. The presence of oxygen in the catalyst preparation is hereby avoided. With such catalysts he has demonstrated high catalytic activity even in systems which contain no oxygen of any kind. Thus, the reduction of diphenyl-diacetylene in hexane and of azobenzene in hexane by hydrogen, in presence of oxygen-free nickel from the cyanide, went with extraordinary velocity. To avoid all objections, Kelber used hexane instead of water as the containing liquid for the hydrogen. Kelber further shows that nickel so obtained has the same characteristics as nickel obtained from oxide, in respect to sensitivity to heat treatment. By reduction at 250°C. the nickel brought about 60cc hydrogen absorption in 5 minutes; on reduction at 400°C., 30 minutes were required for the same gas absorption. Kelber concludes that it is the high temperature which causes a change in surface of the catalyst and that *elementary* nickel can effect the activation of hydrogen.

Willstätter and Seitz suggest that the production of tetrahydro-napthalene or the deca-hydro derivative by hydrogenation of naphthalene in the presence of platinum sponge depends upon the oxygen content of the catalyst.[2] They suggest that direct conversion of napthalene to deca- or tetra-hydro derivatives is possible. With oxygen-rich platinum the tetra-derivative is the preferred product. An attempt is made to justify this view from the exhaustive

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[1] Ber., 57, 136, 142 (1924).

[2] Ber., 56, 1388 (1923). See also, Zelinsky: Ber., 56, 1723 (1923).

experimental data. The tetra-derivative obviously results from hydrogenation of one benzene ring only. Its further hydrogenation only occurs slowly. The deca derivative apparently suffers hydrogenation in both rings simultaneously when little oxygen is present. Is this a case where oriented adsorption occurs, different in the two cases when the platinum catalyst is rich or poor in oxygen?

An interesting contribution to the problem of the nature of nickel hydrogenation catalysts has been made by Schlenk and Weichselfelder,[1] who have succeeded in preparing a hydride of nickel, NiH_2. They prepare it by the interaction of anhydrous nickel chloride on an ethereal solution of phenyl magnesium bromide in an atmosphere of hydrogen. Four equivalents of hydrogen are taken up in the preparation of the hydride, which may possibly be accounted for by the following sequence of reactions

$$2\,\overset{\diagup Ph}{Mg}-Br + NiCl_2 = MgBr_2 + MgCl_2 + [NiPh_2]$$

$$[NiPh_2] + 2H_2 = NiH_2 + 2C_6H_6$$

The hydride is obtained as a black precipitate which, when the solution is decanted, gives, on washing with ether, a black solid. This solid, on decomposition with alcohol and 20 per cent. sulphuric acid, gives a hydrogen evolution corresponding to the formula NiH_2.

$$NiH_2 + H_2SO_4 = NiSO_4 + 2H_2$$

The amount of hydrogen absorbed in the preparation of the hydride is around 3400 volumes per volume of nickel which contrasts strongly with even the maximum values obtained in the adsorption studies at Princeton. Its magnitude seems to rule out the possibility of its being an adsorption complex. The hydride is stable in ether and unstable in presence of alcohol, which fact the authors link with the known ease of hydrogenation by nickel in alcohol solutions and the difficulty obtaining with hydrogenations in ether. The hydride is a good hydrogenation catalyst, not only as to reactions brought about, but also as to the temperature at which it is reactive; it hydrogenated many unsaturated compounds at room temperature. It is, however, a very sensitive catalyst. Oxygen from the air kills its activity for hydrogenation at room temperatures, an observation which is of weight in view of the claims of Willstätter and Boswell already discussed. This active nickel catalyst, at any rate, does not need oxygen for its reaction efficiency.

Definite information as to whether the substance is a hydride or adsorption complex could be obtained from a preparation of the dry substance and a measurement of its dissociation pressure. This measurement, carried out at two temperatures, would give the thermal data for heat of formation, if a compound. Comparison of these with the known data on heat of adsorption of hydrogen on nickel (vide infra) would then materially add to our information on the mechanism of hydrogenation.

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[1] Ber., 56, 2230 (1923).

There is no evidence in the hydrogenation studies of Pease[1] that oxygen is in any way necessary or beneficial in the reaction of hydrogen and ethylene at copper surfaces. Pease's preparations are active some 150° lower than hitherto recorded copper catalysts. His work is of importance in that it associates, for the first time, kinetic measurements with adsorption measurements on one and the same catalyst.

"Because of the known variability among samples of catalytically active material both as regards catalytic activity and adsorptive capacity, it was onsidered vital to obtain measurements of the two properties on the same sample of material. This has accordingly been done. Measurements of reaction velocity have been alternated with determinations of adsorption isotherms on the same sample of catalyst in such a way that sets of measurements of each kind have been "bracketed" by measurements of the other. This has been done in order to take account of any change in activity.

"With respect to the velocity measurements at 0°, the velocity (slope of curve) is greatest with a mixture of $2H_2$:$1C_2H_4$ and least with a mixture of $1H_2$:$2C_2H_4$. With a 50 per cent. mixture the velocity is intermediate between the other two. If the reaction were bimolecular, as the chemical equation suggests it might be, the velocity should be the same for the mixtures of $2H_2$:$1C_2H_4$ and $1H_2$:$2C_2H_4$, and with a 50 per cent. mixture the maximum velocity should be attained. The observed order of the curves suggests rather that the reaction is more nearly unimolecular with respect to hydrogen and independent of the ethylene concentration. An excess of ethylene actually inhibits the reaction rather than causes an increase in velocity.

"When the amount of ethylene is constant, increasing the hydrogen concentration 3.9 times causes the velocity to increase 3.0 times; and when the amount of hydrogen is kept constant, increasing the ethylene concentration 4 times causes the velocity to decrease to 0.6 of its original value; that is, with the same concentration of hydrogen, the reaction velocity increase 1.7 times when the ethylene concentration is decreased to 1/4 of its original value.

It seems to Pease that "a reasonable explanation of these observations can be made in terms of the adsorption theory of catalysis, with the aid of the results of the adsorption measurements. The adsorption of pure ethylene is markedly greater than that of pure hydrogen, being 1.45 cc. at 10 mm. pressure against 0.35 cc. for hydrogen, and 6.80 cc. at 760 mm. against 1.10 cc. for hydrogen. Since, therefore, the adsorption of ethylene at 10 mm. pressure is greater than that of hydrogen even at 760 mm. it is undoubtedly true that from almost any mixture of the two, considerably more ethylene than hydrogen will be adsorbed. Further, if we suppose that those active centers on the catalyst surface which are capable of holding hydrogen are among those which can hold ethylene, it follows that when there is a mixture of the two in contact with the surface they will be competing for these centers and, since the ethylene is the more strongly adsorbed, the hydrogen will occupy relatively few of such spaces. We shall, therefore, be dealing in most cases with a surface largely covered with ethylene, with hydrogen molecules scat-

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[1] J. Am. Chem. Soc., 45, 1196, 2235 (1923).

tered over it here and there. Let us suppose that both ethylene and hydrogen must be adsorbed before reaction can occur. We have concluded that ethylene will usually be present in large excess on the surface, so that its surface concentration will be of secondary importance, so far as it enters directly into the velocity expression. The velocity should, therefore, depend mainly on the amount of hydrogen adsorbed. Other things being equal, the latter will increase with the partial pressure of the gas. It also seems reasonable to believe that as the partial pressure of ethylene, and therefore its adsorption, decreases, the amount of hydrogen adsorbed at a given partial pressure will increase. Since, therefore, we have assumed that the velocity depends upon the amount of hydrogen adsorbed, we may expect it to increase with increasing hydrogen concentration and decreasing ethylene concentration, within limits. These are the relationships found by experiment.

"The average value of the velocity constant is 0.50 at 0° and 1.32 at 20°. The velocity has therefore increased 2.64 times for a 20° rise in temperature. This is equivalent to an average temperature coefficient of 1.62 per 10° rise between 0° and 20°. Such a great temperature coefficient effectually disposes of the possibility of diffusion playing a dominant part in the process. The increase in reaction velocity to be expected from diffusion alone would be about 2 per cent. per 10° instead of the 62 per cent. found. Moreover, if diffusion were a controlling factor, the velocity should depend upon the concentration of that reactant which would diffuse most slowly, namely ethylene, whereas actually it depends upon the concentration of the more rapidly diffusing hydrogen.

"Further information regarding the dependence of the reaction velocity upon the hydrogen adsorption was obtained in some experiments during which the catalyst was poisoned with mercury. No determinations of reaction velocity were made before poisoning but the magnitudes of the adsorptions indicate that the catalytic activity was somewhat greater than that of the catalyst already described. Several adsorption experiments were made and then a little mercury was run up into the stopcock of the manometer and blown into the evacuated catalyst bulb. The quantity of mercury was estimated from the bore of the stopcock to be 0.015 cc. or 200 mg. This would be equivalent to about 20 cc. of vapor at 0° and 760 mm. The bulb was then heated to 200° for ½ hour and evacuated. After cooling, the mercury had disappeared and the catalyst was unchanged in appearance. The adsorptions at 380 mm. of hydrogen and ethylene, respectively, were found to be 3.25 cc. and 8.55 cc. before poisoning and 0.15 cc. and 6.70 cc. after poisoning. The value of dP for a 50 per cent. mixture after poisoning was 0.7 mm. and was estimated to be 200 mm. before poisoning.

"It is evident that the mercury has reduced the adsorption of hydrogen to less than 1/20 of its former value but has reduced the reaction velocity to about 1/200 of its former value. The ethylene adsorption has been only moderately diminished. Here again it is evident that the catalyst must be able to adsorb hydrogen as well as ethylene before it can bring about reaction.

"In the course of the experiments on the catalytic combination of ethylene and hydrogen, the effect on both catalytic activity and adsorptive capacity of partially de-activating a copper catalyst by heating it to 450° in a vacuum was determined.[1] As this gave results which differ somewhat from those obtained by de-activation with mercury, they are also included. The effect of de-activating this sample of copper by heating was in a general way similar to the effect of de-activating the other sample by poisoning it with mercury. The curves have been moved over toward the pressure axis to nearly parallel positions, at the higher pressures at least. The heating has, however, decreased the hydrogen adsorption relatively less than the poisoning and the ethylene adsorption relatively more. Thus, at one atmosphere the decrease in hydrogen adsorption amounts to 70 per cent. while the decrease in ethylene adsorption amounts to 22 per cent. These are to be compared with decreases of 92 per cent. for hydrogen and 14 per cent. for ethylene caused by mercury poisoning. The absolute decreases at one atmosphere are 2.60 for hydrogen and 1.95 for ethylene. It will be seen that these figures are much more nearly of the same order than in the case of copper poisoned with mercury.

"The decrease in catalytic activity in the ethylene-hydrogen combination accompanying these decreases in adsorption amounted to 85 per cent. Just as in the case of the poisoning by mercury, one must go to very low pressures to find a corresponding decrease in adsorption, indicating that *it is the strong (low-pressure) adsorption which is mainly responsible for catalytic activity.*" This last observation seems especially important to the reviewer.

"It is clear from the relative adsorptions of the different gases by active copper that we may at once conclude that ordinary condensation in capillaries is not a sufficient explanation of the results, although it may account for the adsorption of ethane and partially for that of ethylene. The action seems rather to be a specific one between the copper surface and the particular gas. It seems probable, however, that any copper surface will not do, but that the surface must be in a special condition. From the evidence here presented, taken in conjunction with previous experience in the Princeton Laboratories, it would seem that an active copper surface is one which has scattered over it regions containing atoms whose fields are highly unsaturated. This follows from the fact that heating active copper to temperatures as low as 450° caused appreciable sintering besides decreasing the surface activity. Sintering at so low temperatures points to the pre-existence on the surface of atoms of

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[1] Interesting results on the effects of heating active copper to successively higher temperatures have been obtained in the course of this investigation. In the present instance, the catalyst had been prepared at 200°, and heated to 300° after reduction. It had not thereafter been taken above 200°. After the experiments on the active material so obtained had been carried out, the catalyst was heated first to 350° for an hour and then to 400° for ½ hour without a marked change in activity resulting. It was then heated to 450° for one hour after which it was found to have decreased in activity as will be shown. Further heating at 450° for ½ hour was without noticeable effect, however. Similar results were obtained with another catalyst which was eventually heated to 550° to produce a very inactive material. For each rise in temperature a noticeable decrease in activity occurred but further heating at the same temperature was without marked effect. There seems, therefore, to be a stable condition of the surface corresponding to the highest temperature to which it has been heated. All the heatings described above were carried out in a vacuum.

high mobility and therefore in a state of unsaturation. The process of sintering is the process of saturation of these atoms, and since the agency which causes the sintering also decreases the surface activity, it is reasonable to look upon these unsaturated atoms as the cause of this activity. One would look for atoms of this character in surfaces of high degree of curvature—in "peaks", that is to say, on the copper surface—rather than in the "valleys" or capillaries.

"It seems probable that each of these "peaks" can attach more than one molecule of adsorbed gas. Otherwise it is difficult to see how combination of ethylene and hydrogen, for example, can take place as a result of adsorption. As already pointed out, since each hydrogen molecule that is adsorbed apparently displaces an ethylene molecule, the same point on the copper surface cannot hold a molecule of both. The two must, however, be in close juxtaposition if combination is to occur. This can be true only if a given peak possesses more than one possible point of attachment. The activity is, therefore, not due to isolated active atoms scattered over the surface but to groups of these atoms."

At the higher temperatures with less active copper catalysts conditions were somewhat different.

"Measurements of the velocity of combination of hydrogen and ethylene in the presence of copper at 150°, 200° and 250° have shown that in this temperature region the reaction is more nearly bimolecular, in contrast to the combination at 0°, at which temperature the reaction is approximately unimolecular with respect to hydrogen and inhibited partially by excess of ethylene. The more nearly normal character of the reaction at the higher temperatures is believed to be due to the fact that under these circumstances the reacting gases are not measurably adsorbed[1] by the catalyst. The temperature coefficient is much smaller at the higher temperature and is decreasing. By taking into account the decrease of adsorption with rise in temperature as well as the normal increase in velocity of the surface reaction, these facts have been accounted for qualitatively.

In connection with the above views of Pease it is interesting to record that Wright and Smith[2] and Smith[3] have studied the sintering of metals. Smith concludes that:—

(1) Sintering may take place in crystalline and amorphous substances.

(2) The sintering of a crystalline substance is due to a change in the size of the crystals or to the formation of an allotrope.

(3) The sintering of an amorphous material is due to the formation and growth of crystals.

The following sintering temperatures are given:—

Pptd Pt black, 500°; Pd-black, 600°; Pptd Ag, 180°; Pptd Au. 250°; Pptd Co, 200°; Reduced Cu, 500°C; Pptd Cu, 250°; Pptd Fe, 750°; Pptd Ni, 700°.

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[1] It is probably more correct to assume that the adsorption is small and approximately proportional to the partial pressures of each gas. H. S. T.

[2] J. Chem. Soc., 119, 1683 (1921).

[3] J. Chem. Soc., 123, 2088 (1923).

Judged by loss of adsorptive capacity of the reduced metal sintering may take place at much lower temperatures than those recorded above. What this means is that loss of adsorptive power is much the most sensitive index that we have at the present time as to change of surface upon heating.

An attempt has been made by Dougherty and Taylor[1] to gain some insight, by kinetic measurements, into the mechanism of the catalytic reduction of benzene to hexahydrobenzene. The results indicate that the reaction does not occur at all according to the stoichiometric equation, as calculated from gas concentrations, but at rates governed by the distribution of the reacting materials between the catalyst and the gas phase. The trend of the reaction with change of temperature has been studied, and equilibrium values at the higher temperatures have been calculated. The results on the latter show that apparent equilibria in the gas phase, as measured in this way, do not necessarily coincide with those which would be expected on the basis of the ordinary equation representing the reaction. Dehydrogenation becomes marked even in presence of hydrogen above 200°C. Water vapor in small amounts, up to 2 per cent. of the hydrogen volume used in the reaction mixture, had only a slight depressing effect on the reaction velocity. Carbon monoxide in small amounts, about 2 per cent. of the hydrogen volume, had a very marked poisoning effect, particularly at low temperatures of 100° or under. As the reaction temperature was raised the poisoning was less noticeable. In large quantities, however, around 50 per cent. of carbon monoxide, the reaction was completely stopped at 180°. Hexahydrobenzene, at low temperature, 100° or less, had a depressing effect on the reaction velocity. This effect disappeared at higher temperatures, in the neighbrohood of 180°.

The observations show that it is necessary to use great care in making comparative measurements on account of the variability of the nickel catalyst. It was found that different catalysts, although prepared exactly in the same manner, might have quite different activities, and that the activity of a given catalyst changed markedly with time and use. The observations also show that quantitative measurements on a reaction of this kind are difficult due to the fact that the actual reactant concentrations, on which the velocity of the reaction depends, are those on the catalyst surface; and these concentrations may be independent of, or bear a varying relation to, the reactant concentrations in the gas phase.

From experiments at 80° and 90°C it is shown that the temperature coefficient of the reaction measured is approximately 3.1:1.9 or 1.65 per 10 degree rise. This is evidently the temperature coefficient of a chemical reaction as opposed to that of a diffusion process. The experience gained with this kinetic investigation demonstrated the need for both adsorption and kinetic studies on one and the same catalyst.

Continuing his earlier studies[2] in which he showed that the catalytic activity of moistened platinum and palladium in the catalysis of hydrogen-oxygen mixtures is determined as regards velocity by reaction and by the

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[1] J. Phys. Chem., 27, 533, (1923).

[2] 2nd Report p. 814; Ber., 49, 2369 (1916); 53, 298 (1920); 55, 273 (1922).

pre-treatment of the catalyst whether by hydrogen or oxygen, Hoffman,[1] has shown that with iridium, no variation in rate is induced by prior treatment with either gas. The iridium does not seem to adsorb either gas selectively, as demonstrated by measurements of its electrode potential. It is equally efficient in acid or alkaline solution. The catalytic behavior of these three metals for this reaction is therefore definitely associated with the adsorptive capacity of these metals for the gas mixtures. Hoffmann's method of attack is suggestive as a method of study of the still-debated question as to whether oxygen is necessary and indispensable in hydrogenation processes.

Mitchell and Marshall[2] have reinvestigated the work of Anderson[3] on the activation of hydrogen by platinum as revealed by the temperature of reduction of copper oxide. They show that with pure hydrogen no such activation occurs and that Anderson's results are to be attributed to the presence of small amounts of oxygen. The nature of the active hydrogen produced under such circumstances, i.e., with oxygen present, is still uncertain. The authors lean to the conclusion that it is triatomic hydrogen.[4]

Tin has been shown, by Brown and Henke[5], to be an excellent catalyst for the reduction of nitrobenzene to aniline. It is superior to copper at all rates of gas passage but the lowest tried. It is superior to nickel at all but the highest rates. The catalyst is best prepared from the hydroxide by precipitation with sodium carbonate from a stannous chloride solution. Oxidation of the hydroxide prior to reduction increased the efficiency of the resulting catalyst, the lower the temperature of oxidation the better the resulting catalyst. The lower the temperature of reduction of the oxide the better was the resulting catalyst. A catalyst in the form of coarse lumps is better than in the powdered form.

Tin is a new-comer in the ranks of catalysts for reduction. The mechanism of its action is worthy of study. Is it a hydrogenating catalyst or is its action dependent on alternate oxidation and reduction? Both possibilities have their own interest.

Preferential Hydrogenation

Rideal has studied[6] the rate of hydrogenation of cinnamic and phenyl propiolic acids in presence of colloidal palladium. With the metal sol present in large quantities, solutions of the sodium salts of the two acids are hydrogenated at equal speeds, the rate being governed by the rate of hydrogen supply, and proportional to the square of the shaking speed. The reaction velocity is of zero order. For small quantities of sol the velocity is proportional to the concentration of palladium and the phenyl propiolate is hydrogenated at approximately twice the rate of the cinnamate. Above certain critical limits the rate is independent of the shaking speed. The reaction velocity is within wide limits independent of the salt concentration.

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[1] Ber., 56, 1165 (1923).
[2] J. Chem. Soc., 123, 2448 (1923).
[3] Ibid., 121, 1153 (1922).
[4] Cf. Venkataramaiah: J. Am. Chem. Soc., 42, 930 (1923).
[5] J. Phys. Chem., 27, 739 (1923).
[6] Trans. Faraday Soc., 19, 90 (1923).

There appears to be an aging effect with the sols. All sols commence with a velocity curve of zero order and terminate in one of the first order. For active sols the portion not of the zero order is very small whilst for aged sols the portion of the first order is relatively large. For inactive sols the curve is of the first order throughout. Furthermore, with aging, the rate of hydrogenation is diminished considerably.

Rideal attempted to establish the hypothesis that the salt was adsorbed by the palladium sol. He showed that the sol protected by 0.2 per cent. gum arabic undergoes aggregation when treated with the sodium salts. Ten milligrams of a sol aggregated in this manner were filtered through a small filter and washed into a small tube connected to a 10 cc. hydrogen burette. The aggregated sol and filter paper absorbed 4.35 ccs. of hydrogen at 25°C. A duplicate filter paper through which 10 ccs sodium phenyl propiolate had been filtered required a further 1 cc. of hydrogen. Ten mg. of the sol untreated with salt absorbed 1.53 cc. Hence, Rideal concludes, the sol had adsorbed salt equivalent to $4.35-(1+1.53)=1.82$cc. of hydrogen. This corresponds to one molecule of salt to approximately two atoms of palladium, which may or may not be significant. The aging of the sol is attributed by Rideal to reduced adsorptive capacity for the unsaturated salt.

The fact that at low sol concentrations the phenyl propiolate is hydrogenated twice as fast as the cinnamate, suggests to Rideal that the salt is not desorbed from the sol surface until completely saturated and that the phenyl propiolate takes up two hydrogen molecules from the palladium in the same time as the cinnamate takes up one.

A number of investigations indicate, however, that this is not necessarily true for all cases of preferential hydrogenation. Most of the work on hydrogenation of oils involves the possibility of preferential hydrogenation and certain of the researches on the subject indicate its existence. Moore, Richter and van Arsdale[1] indicated that the more unsaturated glycerides were hydrogenated preferentially to the glycerides containing only one double bond. Quite recently, Richardson, Knuth and Milligan[2] have confirmed this conclusion showing that the preferential nature of the process is even more pronounced than had been previously believed. A newer method of analysis of the hydrogenated product revealed, in a typical case the following percentage of saturated, oleic and linolic acid glycerides in the oil before and after hydrogenation.

Cotton Seed Oil	Saturated	Oleic	Linolic Acids
Before Hydrogenation	22.7	27.5	49.8
After Hydrogenation	24.0	67.1	8.9

It is evident that in this experiment the hydrogenation was practically exclusively hydrogenation of linolic acid glycerides and negligible hydrogenation of oleic acid compounds. This would indicate almost exclusive adsorption of the more highly unsaturated glycerides at the nickel surface. The authors found that the selectivity of the hydrogenation appears to be more marked with increasing amounts of catalyst and with increasing temperatures

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[1] J. Ind. Eng. Chem., 9, 541 (1917).

[2] Am. Chem. Soc., September Meeting 1923, Milwaukee, Wis.

up to an optimum in the neighborhood of 200°C. Quantitative measurements on preferential adsorption should prove very interesting in this case. As Bancroft[1] has already pointed out, there are almost no quantitative data on selective adsorption in liquid systems. An intensive study of the field will be fruitful alike to colloid chemistry and contact catalysis.

Dehydrogenation

Dougherty, in the work previously cited, attempted to measure the position of equilibrium in the reaction

$$C_6H_6+3H_2=C_6H_{12}$$

His results were not very conclusive although they did establish the reversibility of the process. He used nickel as a catalyst. Therein, apparently, lay some of his trouble in view of the following conclusions of Zelinsky. Someone ought to repeat Dougherty's work using platinum or palladium instead of nickel.

Zelinsky and Pawlow[2] in studies of the dehydrogenation of cyclohexane with platinum, palladium and nickel show that the efficiency of these catalysts for a given velocity of vapor passage decreases in the order given; dehydrogenation starts as low as 150°C. and is complete around 300-350°C. With platinum and palladium, even as high as 400°C., little or no carbonisation occurs. With nickel, decomposition occurs at a much lower temperature; hence, presumably the very inferior behavior of nickel in comparison with the other two.

Zelinsky[3] show sthat o- dimethyl cyclohexane undergoes dehydrogenation but that 1, 1 dimethyl cyclohexane does not undergo dehydrogenation under such conditions. Zelinsky thinks that 1,1 dimethyl cyclohexane is therefore to be regarded as different from the hexahydro aromatic compounds. Dehydrogenation in Zelinsky's view has therefore a selective character. It is distinctly probable that the free-energy factors concerned will reveal reasons for the absence of dehydrogenation, as they undoubtedly do for the absence of dihydro and tetrahydro derivatives in the hydrogenation of benzene. E. C. Kendall showed some years ago that dihydro-benzene when led through a heated glass tube at 200°C. was completely decomposed to benzene and hexahydrobenzene.

Promoter Action

Pease and Taylor's bibliography of the literature on promoter action[4] showed definitely that little or nothing was known as to the mechanism of promoter action. Beginnings of an attack on this problem are now apparent and elucidation may be expected to follow. It seems essential to take single cases and study them thoroughly—and not to generalise too soon.

One case in which the mechanism of promoter action seems definitely to have been obtained is available in the older literature.

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[1] "Applied Colloid Chemistry," p. 73 (1921).

[2] Ber., 56, 1249 (1923).

[3] Ber., 56, 787, 1716 (1923);

[4] J. Phys. Chem., 24, 241 (1920).

Elissafoff studied[1] the action of glass wool and heavy metal salts cn the velocity of decomposition of hydrogen peroxide both singly and in conjunction with each other. Elissafoff showed that, together, the glass wool and heavy metal salt effected a much more rapid decomposition of the peroxide than would be anticipated on the basis of additive effects. This case is certainly therefore a reaction velocity at the surface and not a diffusion velocity. Were it possible to make adsorption measurements, other modes of decomposition of hydrogen peroxide would possibly be found to be of the same type. Thus with a decomposition velocity of 0.86 in presence of 0.5 g. glass wool in 20 ccs. of peroxide, and one of 1.63 in presence of a 1.54 millimolar solution of copper sulphate without glass wool, a solution with the same copper sulphate concentration plus 0.5 g. glass wool in 20 ccs. gave a decomposition velocity of 10.8; all the velocity units are expressed in arbitrary units. The concentration of hydrogen peroxide was 12 millimolar. In this case, at least the mechanism is apparent. It is known that the decomposition of peroxide takes place at the glass surfaces. It was probable that the copper salt was concentrated at the glass surface and so exercised greater effect. That this was so the following observations indicate clearly. The unimolecular constants for two copper ion concentrations of 1 and 10 millimols per litre were 0.0013 and 0.0023 respectively, in the ratio, therefore of 0:1.77. The amounts of copper salt adsorbed from these solutions by Jena glass powder of the same glass were in the ratio of 1:1.73. It is apparent that the decomposition velocities are proportional to the amounts of adsorbed copper salt.

An informing contribution to the theory of promoter action has been made by Medsforth[2] who has studied the effect of promoters added to a nickel catalyst in the hydrogenation of carbon monoxide and carbon dioxide to yield methane. Reasoning from the simultaneous production of water in the reaction, the addition of catalytic dehydrating agents to the nickel catalyst was made with material increase in the attainable reaction velocity for a given conversion of the reactants. Ceria, thoria, glucina, chromium oxide, alumina, and silica gave a, from 17-fold to 12-fold, increase in velocity over that obtainable with the straight nickel catalyst. Zirconia, molybdenum oxide and vanadium oxide were somewhat less efficient, though still good, promoters. Tin and magnesium oxides, copper and silver metals produced no acceleration over the straight nickel. With the carbon dioxide reaction the increases in velocity effected were somewhat less than those recorded for the monoxide reaction above. The order of efficiency was exactly the same. The order of efficiency is roughly that of oxide catalysts recorded by Sabatier in reference to strict dehydration processes.

In explanation of the activity of the promoters, Medsforth assumes the function of the nickel to be to assist the union of the gases to form a 'complex' or intermediate compound of the methyl alcohol type, probably via formaldehyde. The promoter then functions as a catalytic dehydrating agent on the

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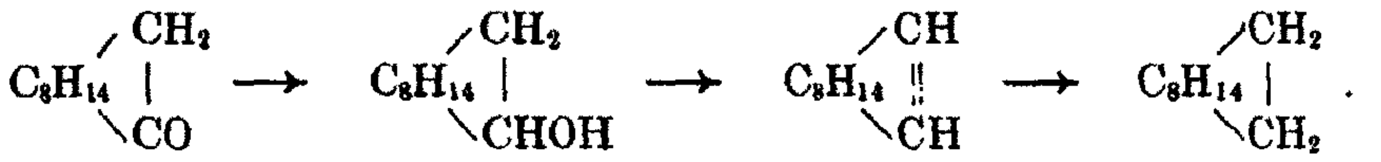
[1] Z. Elektrochem., **21**, 352 (1915).

[2] Chem. Soc., **123**, 1452 (1923).

intermediate compound giving water and a methylene radical whence, immediately, methane results. The promoter assists the known dehydrating action of the nickel. This can be schematised thus

$$CO+2H_2 \longrightarrow H_3C.OH$$

The increased activity of the promoted catalyst is therefore ascribed to increase in (2) and suppression of (1). The combined dehydrogenation and dehydration effected by Ipatiew[1] with a nickel -alumina catalyst whereby the conversion of camphor to isocamphene is effected at 200°C. in one step is cited as supporting evidence



$$C_8H_{14}\begin{array}{l}/CH_2\\ \mid\\ \backslash CO\end{array} \longrightarrow C_8H_{14}\begin{array}{l}/CH_2\\ \mid\\ \backslash CHOH\end{array} \longrightarrow C_8H_{14}\begin{array}{l}/CH\\ \parallel\\ \backslash CH\end{array} \longrightarrow C_8H_{14}\begin{array}{l}/CH_2\\ \mid\\ \backslash CH_2\end{array} .$$

The several steps of this process can be conducted singly with the single catalysts though less efficiently.

Medsforth calls attention to an important feature of promoter action which he has noted, that of selective promotion. It would appear that when two reactions, both capable of being accelerated, take place at the same time in the presence of the same catalyst and the same promoter, that which is normally slower is accelerated to a greater comparative degree than that which is normally the faster. Support for this statement was obtained in the observation that when carbon monoxide and steam react in the presence of nickel and nickel promoters, whilst carbon dioxide and hydrogen are the main products, methane is also formed, the quantity of which is greater when, for example, alumina is present than when nickel alone is used. Similarly, in the production of methane from carbon monoxide and hydrogen, more carbon dioxide is formed as a by-product due to the simultaneously occurring water gas reaction, when promoters are added to the nickel catalyst, than if this latter is used alone.

In discussing the applications of his dehydration hypothesis Medsforth reviews several cases of promoter action. For catalysis of the water gas reaction with iron oxide as catalyst it is significant that the promoters among the most effective are hydrating agents and oxygen carriers. The action of ceria-thoria in the incandescent mantle may also be in part due to combined oxygen carrier-dehydration effectiveness.

As a temporary classification of promoters for purposes of discussion Medsforth gives the following:

(1) The promoter decomposes intermediate compounds formed by the catalyst.

(2) The promoter causes the reacting substances to combine, the resulting intermediate compound being decomposed by the catalyst.

(3) The promoter adsorbs or combines with one of the reacting substances producing a greater concentration of the latter at the catalyst surface.

Further contributions to the problem are promised.

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[1] J. Russ. Phys. Chem. Soc., 44, 1695 (1912).

The origin of the carbon dioxide in the methanation process has been elucidated by Armstrong and Hilditch[1] who have shown that when purified water gas is passed over nickel at 200-300°C. the predominating reaction is $2CO+2H_2=CO_2+CH_4$. The reaction is regarded as the sum of two reactions

$$CO+H_2O=CO_2+H_2$$
$$CO_2+2H_2+2H_2=CH_4+2H_2O.$$

the former of which is regarded as occurring in the same manner as the reaction in presence of copper previously studied by them[2], namely via formic acid $CO+H_2O \longrightarrow HCOOH \longrightarrow H_2+CO_2$. With cobalt, the reaction commences at a lower temperature, 180°C., but the above reaction is subsidiary to the main methanation process $CO+3H_2=CH_4+H_2O$. Silver is inert, iron almost so, platinum and palladium of minor activity. Mixed catalysts were less efficient than the single catalyst. With nickel at increasing pressures up to 6 atmospheres the minimum temperature of interaction rises. The reaction yielding carbon dioxide and methane produces more methane from water gas than any of the other reactions. It may therefore have value as a means of increasing methane content or lowering carbon monoxide content of town's gas. The authors state that CO_2+H_2 goes directly to methane and gives no carbon monoxide, so that partial reduction is apparently not taking place. This is at variance with some observations made in the laboratories of the Munitions Inventions Dept., in England, during the war, where methane prepared from carbon dioxide and hydrogen contained a small percentage of carbon monoxide.

In contrast to the conclusions of Medsforth cited above, Armstrong and Hilditch[3] conclude, with regard to the 'promotion' of a straight hydrogenation process, the simple addition of hydrogen at an unsaturated linkage, in presence of nickel, alumina, silica, oxides of iron and magnesium being employed as promoters, that the stimulation observed can be satisfactorily explained on the basis of increased available catalytic surface of the nickel. There is some evidence of the removal or adsorption of catalyst poisons (sulphates in the precipitated oxides, or traces of impurities in the oil hydrogenated); but these appear as minor influences compared to the effect on the extent of surface of nickel produced. They have been able to make an appreciably less amount of reduced nickel effect the same amount of action whatever the extent of the catalyst in alumina or other 'promoting' oxide.

Armstrong and Hilditch[4] showed that the presence of sodium carbonate effectively promotes the hydrogenation of phenol at nickel surfaces, About 25 per cent. by weight of nickel appears to give the maximum effect. In the presence of carbonate the reaction rate is more nearly linear than in the absence of the carbonate. This factor suggests that the function of the promoter is a protective one to the catalyst, keeping it free of inhibiting impurities.

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[1] Proc. Roy. Soc., 103A, 25 (1923).

[2] Proc. Roy. Soc., 97A, 265 (1920).

[3] Proc. Roy. Soc., 103A, 586 (1923).

[4] Proc. Roy. Soc., 102A, 21 (1922).

The promotion of nickel by the addition of copper,[1] Armstrong and Hilditch ascribe to the influence of the copper on surface area.

Catalytic Oxidation and Promoter Action

The enhanced activity of manganese dioxide-copper oxide (Hopcalite) mixtures as catalysts for carbon monoxide oxidation has received further attention this year, and progress towards the solution of the mechanism in this case has been made.

Bray and Almquist[2] state that their results indicate that the mixture, 60 per cent. MnO_2, 40 per cent. CuO is but slightly more active than other mixtures, and that basic copper carbonate as a component has little if any advantage over copper hydroxide.

The following theory of the mixture effect in this case proved useful throughout their experimental work.

"By the action of carbon monoxide and oxygen a protective film is formed on the catalyst which interferes with further action, unless it can be rapidly desorbed as carbon dioxide. The film builds up to a lesser extent for mixtures than for the one-component catalysts at the same temperature. The slow limiting reaction may be the rate of desorption of carbon dioxide or the rate of a transformation within the film. We could stop with the statement that this is a question of the structure of the catalyst, but it seemed worth while to seek an interpretation in terms of valence theory.

"The porous granules are believed to consist of a network of chains of atoms held together by valence forces.[3] The forces that come into play at or in the film are also valence forces. When the catalyst contains the two oxides, they will tend to neutralize each other's valence forces, since they differ in basicity or polarity, and the strength of the valence forces at the film may be expected to be less than for a one-component catalyst. In other words, an increase in the rate of desorption, or increase in the rate of a reaction within the film, is attributed to what may be considered a partial chemical reaction between the two oxides.

Whitsell and Frazer[4] conclude that "manganese dioxide in Hopcalite mixtures is the initial cause of the oxidation at low temperatures. The active preparations are able to oxidize carbon monoxide extremely rapidly either catalytically or at the expense of their own oxygen. The analytical data show that these active samples have a very low potash content, less than 0.5 to 1.0

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[1] Cf. Dewar and Liebmann: U.S.P. 1,268,692; 1,275,405.

[2] J. Am. Chem. Soc., **45**, 2305 (1923).

[3] Compare Langmuir: J. Am. Chem. Soc., **38**, 2285 (1916).

The formation of the firm porous granule from the hydrated oxide or oxides may be thought of as follows. Each hydrated oxide is precipitated in the form of minute particles, the size of which is determined by the method of precipitation, but is greater than molecular dimensions. The filter cake, before it is dried consists of particles surrounded by film of water, which enable the relative positions of the particles to be easily changed for example, in a kneading process. In the preliminary drying as the water is slowly expelled, the particles are gradually drawn together, and in many places contact is sufficiently close to allow valence forces to come into play between the molecules of different particles. The plastic material has now been transformed into a solid. Finally, as the water of hydration is gradually expelled, the body becomes porous.

[4] J. Am. Chem. Soc., **45**, 2848 (1923).

per cent of K_2O, while the partially active sample initially tried contained very likely 3 per cent. or more, as has been shown by other investigators (English). These samples were otherwise quite alike as to physical structure. The commercial sample after partial reduction was able to take up enough oxygen at an elevated temperature to restore its activity for a time. When it was more completely freed from potash it was able to take up oxygen fast enough to become completely catalytic at lower temperatures. This points to a mechanism of alternate reduction and oxidation of the catalyst. The efficiency is quite evidently dependent on the nature of the active surface as well as on its extent. A sample of preparation No. 4, for example, which had been ignited too strongly, on evaporation became quite dense, resembling the natural product and was entirely inactive, although alkali-free. This meant a packing and possibly a total change of structure of the material, and a reduction and probably alternation of the nature of the surface but without destruction of the porous structure. The "promoted", Hopcalite, sample is active, although it still may contain 1.74 per cent. of K_2O. To state with certainty the effect of the cupric oxide on the mixture it would be necessary to have data on a sample of manganese dioxide containing this amount of alkali. If the alkali is all associated with the manganese dioxide, as the Hopcalite is 60 per cent. of manganese dioxide, the latter actually contains 2.90 per cent. of K_2O. As a sample of manganese dioxide containing this much impurity would hardly be completely catalytic alone it seems that the cupric oxide does show promoter action. It is still possible that it cuts down the adsorbed alkali or affects the way it is held so that its poisonous effect is annulled. On the other hand, both cupric and manganous ions are catalysts in other oxidation processes. These adsorbed ions may, therefore, act as oxygen carriers to the carbon monoxide. The activity seems to be intimately connected with the ability and rapidity with which the substances can take up oxygen, which may be caused by the rapid shifting of electrons in manganese atoms, so the poison or promoter may affect the stray field or the atomic or molecular configuration of the catalyst itself.

"Attention is next called to the manganese-oxygen ratios in the samples. Here as in the previous investigations the loss of oxygen by manganese dioxide is noticed even at room temperatures and in a wet sample, indicating a dissociation pressure of oxygen in the pure manganese dioxide greater than the partial pressure of the oxygen in the atmosphere. English finds that these oxides behave as solid solutions, the oxygen pressure varying with the composition of the mixture; this is similar to the conclusions of Sosman and Hostetter[1] in the case of the oxides of iron. The action of promoters and poisons may be due to their presence as constituents of such solutions. The fact that the mixtures lose oxygen at room temperature shows that they have a dissociation pressure greater than the oxygen in the air, and the activity because of this is greatly increased by the fineness of division of the particles.

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[1] J. Am. Chem. Soc., 38, 807 (1916).

The molecules are at a point where electron changes occur with great rapidity, and oxygen evaporates and condenses as readily as molecules do in the case of a liquid at its boiling point.

The rapidity of oxidation of carbon monoxide (the time of contact is of the order of 0.01 second, comparable to that in the oxidation of ammonia) shows that the monoxide is not held very tightly as such. If it were, it would be its own poison. Failure to effect desorption of carbon monoxide as such from manganese dioxide points to a rapid re-arrangement and reaction. That carbon monoxide may be adsorbed is shown by the experiments with the less active cupric oxide. The course of the reaction would be, then, adsorption and simultaneous oxidation or its adsorption by the catalyst; desorption of the carbon dioxide or its adsorption by capillary condensation in case the catalyst were not already saturated; and finally reoxidation of the catalyst. The carbon dioxide is inert and chemically inactive and therefore does not poison the catalyst except by mechanically covering the surface and preventing contact of the reactant with the catalyst surface.

Benton[1] attacked the problem by studying adsorptions of carbon monoxide (and hydrogen) by various oxide catalysts and mixed oxides.

"It will be observed that the order of adsorption of the different gases is the same on each of the oxides. Carbon dioxide is most extensively adsorbed, carbon monoxide is next, followed by nitrogen, then oxygen, while hydrogen is least adsorbed. The order of decreasing boiling points is carbon dixoide, oxygen, carbon monoxide, nitrogen, hydrogen. The corresponding order for melting points is carbon dioxide, carbon monoxide, nitrogen, oxygen, hydrogen; in other words, the same as the order of adsorption. This relation holds because the adsorptions are largely of the secondary valence type. A glance at the tables will show that for active oxides, the adsorption of carbon monoxide is abnormally large, and this abnormality increases at higher temperatures. Thus at 0° and above, carbon monoxide is held on active oxides mainly by primary adsorption, while at low temperatures the adsorption is largely secondary.

"Although the effective surface areas of these oxides are unknown, so that it is not possible to compare them in terms of adsorptions per unit area, yet this difficulty may be overcome to some extent by using ratios of the volumes of different gases adsorbed by each oxide.

"The ratio of carbon monoxide adsorbed at $-79°$ to carbon dioxide adsorbed at 0° is nearly the same for each adsorbent. This suggests that both of these cases involve mainly secondary adsorption. For acidic oxides either the adsorption of oxygen is abnormally great, or that of carbon dioxide is abnormally small. Ordinary chemical considerations suggest that the latter alternative is the correct one. Obviously, however, the adsorptions in these cases are principally of the secondary valence type. The deviations from complete uniformity could perhaps be attributed merely to quantitative,

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[1] J. Am. Chem. Soc., 45, 887, 900 (1923).

rather than qualitative differences in the forces involved, yet there is no reason why certain of these oxides should not adsorb carbon dioxide or oxygen to some extent by primary valence forces.

The large differences in the ratios of carbon monoxide at 0° to carbon dioxide at 0°, or of the monoxide at 0° to oxygen at 0°, show the specific nature of carbon monoxide adsorption at this temperature. If the assumption be made that, with adsorption by silica, primary valence forces do not enter the process appreciably, these ratios furnish a means of distinguishing quantitatively between the primary and secondary adsorptions. On this basis the secondary adsorptions of carbon monoxide at 0° should in all cases be 1.77 times as great as the oxygen adsorptions, or 0.08 times as great as the carbon dioxide adsorptions. In Table I are given the secondary carbon monoxide adsorptions at 0°, calculated in this way, together with the observed total adsorption. The last two rows contain the primary adsorptions, obtained by subtracting the secondary adsorptions from the total.

TABLE I

Primary and Secondary Adsorption of Carbon Monoxide

		Co_2O_3	Hopcalite	CuOIII	MnO_2	Fe_2O_3	V_2O_5	SiO_2
Total CO at 0°		?	4.42	1.66	1.90	1.62	0.053	2.662
Secondary calc.	O_2 at 0°	0.47	0.44	0.23	0.60	0.85	0.055	(2.662)
from	CO_2 at 0°	0.82	0.49	0.36	0.69	1.42	0.030	(2.662)
Primary,	O_2 at 0°	?	3.98	1.43	1.30	0.77	0.00	(0.0)
from	CO_2 at 0°	?	3.93	1.30	1.21	0.20	0.023	(0.0)

The two methods of calculation do not give identical results because, as already mentioned, the adsorptions of carbon dioxide and of oxygen by certain of these oxides cannot be regarded as purely secondary. The two methods do, however, place the oxides in the same order with respect to the primary adsorption of carbon monoxide. Similar results are obtained for hydrogen, but since the adsorptions of this gas are very small, the relative precision of the measurements is much less than with carbon monoxide. It should be noted that these calculations are quite independent of any assumptions with regard to the relative effective surface areas. It has, however, been tacitly assumed that a large primary adsorption has no effect on the secondary capacity. If, as seems likely, this is not strictly true, all the secondary adsorptions in Table I should be diminished, and the primary adsorptions therefore increased, by a certain small fraction of the calculated primary adsorptions. Obviously this correction could not alter the order of the oxides with respect to primary adsorption.

The order of chemical reactivity of these oxides toward hydrogen and carbon monoxide[1] is the same as the order in which they are listed in Table I and, therefore, the same as that of the primary adsorption, with the exception of manganese dioxide and cupric oxide, which are reversed. This parallelism

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[1] As determined in these experiments from the slope of the volume-time curves, previously described. Cf. Wright and Luff: J. Chem. Soc., 33, 1, 504 (1878).

suggests that primary adsorption is an intermediate stage in the reduction of these oxides, at least at comparatively low temperatures. In other words, carbon monoxide, on coming in contact with a readily reducible oxide, is almost instantly adsorbed by primary valence forces, forming a surface complex which can decompose either into the original substances or into the reduction products, depending on the conditions. At higher temperatures the rate of decomposition of the surface complex into the reaction products is extremely rapid but at comparatively low temperatures it becomes so slow that at any instant a large fraction of the surface is covered with this adsorbed layer of carbon monoxide molecules. At still lower temperatures carbon monoxide is adsorbed less and less by primary valence, and more and more by secondary. The latter, however, is not a preliminary stage in the reduction, except in so far as a primary valence union results from the secondary type by a shift of electrons.

Relation between Extent of Adsorption and Catalytic Activity

The catalytic behavior of these oxides in the combination of carbon monoxide and oxygen has been investigated[1] by the Chemical Warfare Service, and also to some extent by the Munitions Inventions Department in England. The order of catalytic activity was found to be Hopcalite, cobalt sesqui-oxide, cupric oxide, manganese dioxide, ferric oxide. Vanadium pentoxide was not investigated and therefore cannot be placed with certainty, but it is known[2] that silica comes at the end of the list. All the oxides whose adsorptive capacities were measured were prepared and dried by the same processes as those used for the samples whose catalytic activity had been determined, except in the case of Hopcalite. Hopcalite similar to that used for the adsorption experiments was found[3] to be less than 100 per cent efficient at temperatures below 40°, so that this mixture must be put in second place, after cobalt sesquioxide, in the activity series. For convenience of comparison, these facts are collected in Table II, together with the results of the adsorption measurements. In the table the properties in question decrease from left to right.

TABLE II

Comparison of Catalytic Activity and Adsorption

Catalytic activity	Co_2O_3, Hopcalite, CuO, MnO_2, Fe_2O_3, V_2O_5(?), SiO_2
Secondary adsorption	SiO_2, Fe_2O_3, MnO_2, Co_2O_3, Hopcalite, CuO, V_2O_5
Primary adsorption of CO	Co_2O_3, Hopcalite, CuO, MnO_2, Fe_2O_3, V_2O_5, SiO_2.

The most obvious conclusion to be drawn from Table II is that no connection whatever exists between the extent of secondary adsorption and catalytic activity for carbon monoxide oxidation. The primary adsorption of carbon monoxide, however, is in exactly the same order as the catalytic activity.

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[1] Rideal and Taylor: Analyst, 44, 89 (1919); Rideal; J. Chem. Soc., 115, 993 (1919); Lamb, Bray and Frazer: J. Ind. Eng. Chem., 12, 213 (1920); Merrill and Scalione: J. Am. Chem. Soc., 43, 1982 (1921).

[2] Bodenstein and Ohlmer: Z. physik. Chem., 53, 166 (1905). This statement is supported by new experiments with precipitated silica.

[3] In an experiment by H. S. Taylor.

This means that if the total adsorptions as measured are compared with the catalytic activity, no relation will appear, because the adsorption consists in general of two different phenomena, only one of which has a bearing on the activity. The powerful force fields at the surface of silica, indicated by its high melting point, produce a comparatively high adsorption of all gases, but it is a secondary valence adsorption and consequently leads only to weak, if any, catalytic effects. Charcoal, probably the best adsorbent known, catalyzes few reactions, because the adsorptions in question are largely secondary. Charcoal does catalyze the chlorination of natural gas as well as a number of oxidation reactions, but the adsorption of oxygen certainly is of the primary valence type, as is probably also that of chlorine. Secondary adsorption appears to produce, at the most, only comparatively slight activation of the adsorbed molecules.

Concerning the actual chemical composition of oxide oxidation catalysts Weiss, Downs and Burns[1] make an interesting contribution. They show that in presence of benzene-air mixtures of definite concentration at a given temperature the catalyst is, in reality, a definite ratio of two oxides, V_2O_5 and V_2O_4. At 400°C. with 14 parts by weight of air to 1 part by weight of benzene the catalyst after use was 94.3 per cent V_2O_5 and 5.7 per cent V_2O_4 while before use it was a mixture of 60 per cent V_2O_5 and 40 per cent. V_2O_4. When the benzene concentration was increased the percentage of V_2O_5 in the used catalyst fell. With 2.2 parts of air to one of benzene the percentage had fallen to 9.1 per cent. V_2O_5. This adjustment of the oxide ratio to gas concentrations suggests strongly that the mechanism of the catalysis involves an oscillation between V_2O_5 and V_2O_4. At temperatures above 400°C. with any given gas concentration the proportion of V_2O_5 will progressively decrease. The authors have found that complete combustion also increases at the expense of the partial oxidation product. The opposite is true of the lower temperature range. Hence, the authors conclude that the proportion of complete combustion is not dependent on the ratio of V_2O_5 to V_2O_4 but upon some other factor, such as the activation of the reacting substances.

Dunn and Rideal[2] studying the oxidation of nickel sulphide by gaseous oxygen in aqueous solutions show that the process is a heterogeneous surface reaction occurring in stages with the intermediate production of basic salts. The oxidation is markedly accelerated by soluble vanadium compounds. The catalytic effect is ascribed to colloidal $V(OH)_3$ and is greatest in weakly acid solutions.

Adsorption and Catalysis

The general conclusions of the work at Princeton have been summarised in a communication[3] to the Colloid Symposium from which the following extracts are quoted.

Adsorption is a condition precedent to catalytic change. The data obtained by Taylor and Burns on hydrogenation catalysts showed marked adsorption of gases which take part in hydrogenation processes. Low ad-

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[1] Ind. Eng. Chem., 15, 965 (1923).

[2] J. Chem. Soc., 123, 1242 (1923).

[3] Colloid Symposium Monograph, p. 101 et seq., Madison (1923).

sorptive capacities were found with relatively inert catalysts. Pease studied this relationship in detail with ethylene and hydrogen on copper showing that high catalytic activity was paralleled by high adsorptive capacity for both gases. Pease further showed that by suppressing the adsorption of hydrogen by partially poisoning the copper catalyst with mercury the catalytic activity was likewise suppressed. Adsorption of both reactants is therefore a condition precedent to efficient catalysis in this case. Benton showed marked adsorption of carbon monoxide and, to a lesser degree, oxygen by oxide catalysts capable of effecting the combination of these gases. Dougherty and Taylor demonstrated the adsorption of benzene vapors by nickel. Taylor, Benton and Dew[1] have measured ammonia adsorption on a variety of metals which catalyse the decomposition of ammonia. Taylor and Beebe[2] have shown that hydrogen chloride is adsorbed by the copper chloride catalyst of the Deacon chlorine process.

The Form of the Catalyst and Adsorption:—The extent of adsorption per unit weight of catalyst is determined by the method of preparation, distribution on inert supports or by subsequent treatment of the surface by catalyst poisons or by heat treatment.

Variation in adsorptive capacity with variation in the methods of preparation, may be illustrated from the work on copper, on nickel and on an oxide such as cupric oxide. These results are strikingly displayed in the following tables.

Adsorptions on Copper

Temperature of Reduction of CuO.	Nature of CuO	Time required for Reduction	Adsorption per 100 g. Cu at 0°C and 760mm H_2	C_2H_4	Observers
250°C.	Ignited nitrate	Few hours	0.2	2.85	T and Bu
200°C.	Kahlbaum's granules	30-40 hrs.	3.0	8.0	P
150°C.	Kahlbaum's	4 days	15.5	——	T and D

Adsorptions on Nickel

Temperature of Reduction of NiO.	Nature of NiO	Time required for Reduction	Adsorption H_2 per 100 g. at 25° C. and 760 mm.	Observers
300°C	Ex nitrate	12 hours	47 ccs.	T and Bu
300°C	Ex nitrate	?	70 ccs.	G and T
300°C	Ex nitrate	2 days	130 ccs.	T and Be

This catalyst probably more finely divided than the first two.

Adsorptions on CuO

Nature of CuO	Adsorption per 100 g. CuO at 25°, 760 mm. CO_2	O_2	CO	Observer
Strong ignition of Cu	0.015	0.005	0.012	Benton
Calcination of Nitrate	0.132	0.00	0.180	Benton
Ppt$^{\underline{n}}$ of hydroxide	36.2 (0°C)	1.0 (0°C)	13.3 (0°C)	Benton

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[1] Unpublished work.

[2] J. Am. Chem. Soc., 46, 45 (1924).

The effect of a catalyst support on the adsorptive capacity per unit weight of catalyst is well illustrated by the work of Gauger and Taylor with nickel from the calcined nitrate and with nickel spread on a diatomite brick.

Catalyst	H_2 adsorbed per g. Ni at 750 mm. and						
	25°	80.5°	175°	184°	200°	218°	250°
Unsupported Ni	0.69	0.63		0.53		0.84	
Ni on diatomite			5.2		5.1		4.73

The best quantitative data on the effect of poisons on catalyst adsorption obtained in the Princeton work are those obtained by Pease on copper. Adsorptions of hydrogen and ethylene on 100 g. Cu were made before and after the catalyst was poisoned with mercury, the quantity of poison being estimated at 200 mg.

	Adsorption at 0°C., and 380 mm.	
	H_2	C_2H_4
Before poisoning	3.25 cc.	8.55 cc.
After poisoning	0.15 cc.	6.70 cc.

The striking disparity in the influence of the poison on the adsorptive capacities of the two gases is worthy of study. The hydrogen adsorption is reduced to less than 5 per cent. of its initial value. The ethylene adsorption, on the other hand, is still approximately 80 per cent. of its initial value. At the present time, we are inclined, taking these data in conjunction with others on the effect of heat to be presented below, to attribute this phenomenon to differing capacities of surface atoms to adsorb hydrogen and ethylene. The mercury vapor, on this hypothesis, would be preferentially adsorbed on those portions of the surface which have hydrogen-adsorbing capacity.

Heat treatment of an active catalyst preparation is now our standard method of preparing catalysts with controlled adsorptive capacity or catalytic activity. From a variety of experiments, we may choose the following as indicative of the effect produced by heat treatment.

Catalyst	Heat treatment	Adsorption at 0° and 760 mm.		Observer
		H_2	C_2H_4	
A. Active Cu. 100 g.	No heat beyond reduction of oxide at 200° C.	3.70 cc.	8.45 cc.	Pease
B.	A. heated to 450°C. for 1.5 hours	1.15	6.85	Pease
C. Active Ni. 27 grms.	Obtained by reduction of oxide at 300°C.	35		Beebe
D.	C. heated at 400°C. for 4 hours.	16		Beebe

The same abnormal depreciation of the hydrogen adsorption on copper is to be noted here as in the poisoning experiments. This evidence we would interpret thus: A smaller fraction of the surface is capable of adsorbing hydrogen than ethylene. The greater adsorptive force required by surface atoms in order to hold hydrogen is, in our view, to be regarded as possessed by those atoms in the surface which have a greater degree of freedom from the normal crystal lattice of the solid catalyst. These atoms have a lesser fraction of their electron shells surrounded with neighbouring copper atoms. They therefore possess a greater surface energy. They would also possess a higher vapor pressure. With the moderate heat treatment accorded to the catalyst in the above mentioned cases these atoms distil to positions of lesser surface energy more readily than do atoms of less freedom in the solid lattice. It is these atoms of high surface energy which will be most affected by heat treatment; they should be the preferred positions of attachment of catalyst poisons. *The Specificity of Catalytic Adsorption*:—Freundlich points out[1] that "since in adsorption by charcoal, the physical characteristics of the adsorbed gas are of far more importance than the specific effect between gas and adsorbent, it is not remarkable that also with adsorption by different adsorbents the influence of the special properties of the adsorbent is strongly suppressed (stark zurücktritt). It can be said with a certain approximation that oftentimes gases are adsorbed, independently of the nature of the adsorbent, in the order of their compressibilities."

This thesis is entirely inapplicable to catalytic adsorption. The ratio α_1/α_2 for the adsorption of two gases by adsorbents A, B, C, etc., which on the basis of Freundlich's statement would be approximately constant for each adsorbent, A, B, C, etc., may vary quite widely for catalytic adsorbents. The large differences in the ratio of adsorption of carbon monoxide at 0°C. to carbon dioxide at 0°C. obtained by Benton show the specific nature of carbon monoxide adsorption at this temperature for a variety of oxide catalysts.

	Hopcalite	CuO	MnO_2	Fe_2O_3	V_2O_5	SiO_2
$\frac{\alpha_{CO}}{\alpha_{CO_2}}$	0.72	0.37	0.22	0.09	0.14	0.08

The same ratio at 25°C. for a few metallic catalysts is obtainable from Burns' measurements

	Cu.	Co.	Fe	Pd	Pt Black
$\frac{\alpha_{CO}}{\alpha_{CO_2}}$	10.0	3.6	2.8	288	10.6

It is very evident, since this ratio varies from 0.1 to 300, that the Freundlich relation is entirely untenable for such cases as we are dealing with here. It has only a very circumscribed applicability, namely, to chemically inert adsorbents and easily liquefiable gases. A most striking case of the specific behavior of catalytic nickel is to be found in Freundlich's book (p. 203) in his discussion of some unpublished work by Zisch on the decomposition of nickel carbonyl at nickel surfaces. As Freundlich points out one might expect, on the basis of the higher critical temperature of nickel carbonyl as compared with carbon monoxide, a much higher adsorption. Actually, carbon monoxide, even in minute quantities, exerts a powerful retarding action on the decomposition, indicating marked preferential adsorption. Our present knowledge with respect to the structure of nickel carbonyl and its stable configuration on

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[1] "Kapillarchemie." 2nd Edition, p. 178 (1922).

the basis of the Lewis-Langmuir theory of structure immediately suggests the chemical reasons for this specificity of adsorption, unexplainable on the basis of physical characteristics. Other striking variations in ratio of adsorbed gases are to be found in the records of the Princeton work. Consideration of the preceding section on the influence of catalyst poisons and of heat treatment on adsorptive capacity will show furthermore that the ratio of adsorption of gases by a single catalyst is also variable with variation in the preparation and of treatment of the catalyst. The rule as to nonspecificity of adsorbents must be discarded when cognisance is taken of the data on catalytic adsorbents.

Specificity of Adsorption and Specificity of Catalytic Activity:—The influence of specific adsorption in determining specific catalytic activity is best demonstrated by work dealing with the preferential catalytic combustion of carbon monoxide admixed with hydrogen. As is well known, metallic oxides may be used to catalyse the combination of carbon monoxide and oxygen present in equivalent concentrations in a large excess of hydrogen. The mechanism of this preferential oxidation is at once apparent from the adsorption ratio of the two gases at atmospheric pressure on various oxides at -79°C., as determined by Benton.

Oxide =	Hopcalite	MnO_2	CuO	Co_2O_3	Fe_2O_3	V_2O_5	SiO_2
$\frac{\alpha_{CO}}{\alpha_{CO_2}}$	33	100	34	19	35	17	28

For exact comparison with preferential combustion data adsorptions at low partial pressures of carbon monoxide should be compared with those of hydrogen at approximately atmospheric pressure. The results cited, however, show marked preferential adsorption of carbon monoxide. With metals the preferential nature of the combustion process is less pronounced. With nickel and platinum the hydrogen is freely consumed; with copper a fair preferential combustion may be attained. Note the following data on adsorption ratios of the two gases at various temperatures and atmospheric pressure and contrast them with the oxide data.

	Ni	Pt. Black	Cu
$\frac{\alpha_{CO}}{\alpha_{H_2}}$	0.87 (184°)	3.3 (100°)	12

The data cited are also of interest in connection with the problem of specificity of adsorbent discussed in the preceding section.

Variation of Adsorption with Pressure and the Heat of Adsorption:—As is well known, the variation of adsorption with pressure on adsorbents such as charcoal is approximately given by the Freundlich equation

$$\alpha = k\,C^{1/n}$$

where α = amount adsorbed, k and n are constants the latter being always equal to or greater than unity.

The data on the variation of adsorption with gas pressure with metallic catalysts as adsorbents are few; some of these, however, show striking characteristics. Gauger and Taylor's data on the adsorption isotherms of hydrogen on nickel are the most completely studied thus far. The curves obtained at a variety of temperatures 25-305°C., show the characteristic shape of normal adsorption isotherms so far as absence of discontinuities indicative of compound formation are concerned; they show, however, this distinction that at a certain pressure at each temperature, a definite saturation capacity of the surface is apparently reached. This saturation capacity is reached at very low partial pressures, 40 mm. at 25°C., and approximately 250 mm. at 305°C. Beyond these pressures, further increase in gas pressure up to atmospheric pressure (i.e. $\frac{760}{40} = 19$ fold increase in pressure at 25°C.) adds to the amount of gas adsorbed so little as to be within the error of measurement. The same observation is true in the recent results of Pollard[1], employing hydrogen, and, to a less extent, carbon monoxide on platinum. The amount of adsorbed hydrogen in this case does not sensibly increase beyond a gas pressure of 100 mm. Pease's data on the adsorption of hydrogen by copper show a similar if less pronounced attainment of saturation capacity. The adsorption of hydrogen at 380 mm. pressure was 90 per cent. of that at atmospheric pressure. Similar behavior with respect to carbon monoxide on copper is shown in some data obtained by Jones and Taylor on the adsorption isotherms of carbon monoxide and carbon dioxide on copper at 0°C. and 80°C. Earlier work on adsorbents of the charcoal type has not indicated the attainment of saturation capacity of the surface even at pressures well beyond atmospheric pressure. A further distinction is also noticeable. Gauger and Taylor's results show that the adsorptive capacity of hydrogen on nickel at saturation is, at 305°C., as much as 60 per cent. of the saturation capacity at 25°C. Some recent data obtained by Dew on copper show adsorptions of hydrogen in the ratio of 10 to 8.7 at 0° and 110° C. and atmospheric pressure. Contrast this with the data concerning adsorption on charcoal. The adsorption of carbon monoxide at 400 mm. and 46°C. is only 8 per cent. of that at −78°C., this temperature interval being about the same as that obtaining in Dew's case and less than one-half of that recorded above with nickel and hydrogen. The adsorption of carbon dioxide on charcoal at 150°C. and atmospheric pressure is less than 7 per cent. of that at −78°C. These striking differences both in the pressures at which saturation is attained and in the variation of adsorption with temperature are undoubtedly of fundamental importance in the study of catalytic adsorbents.

Data on adsorption isotherms may be utilised to evaluate the heat of adsorption of gases on the adsorbent surface. Gauger and Taylor using the minimum pressures at which saturation is reached at the several temperatures and substituting these in the equation

$$\lambda = 4.57 \frac{T_1 T_2}{T_2 - T} \log \frac{P_2}{P_1}$$

obtained a value for, λ, the heat of adsorption of 2500 calories. This cal-

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[1] J. Phys. Chem., 27, 365 (1923).

culation is in error since the equation should be applied[1] to the pressures P_1 and P_2 at which *equal* amounts of gas are adsorbed, or in other words, equal fractions of the surface are covered. The data of Gauger and Taylor do not lend themselves readily to such computations if accuracy is desired, as the pressures at which equal fractions of the surface are covered at different temperatures are small and consequently most liable to error. From the best available data however, calculated in the correct manner, a value for the isosteric heat of adsorption of 15000+3000 calories was obtained.

Rideal and Thomas[2] showed that the adsorptive capacity of three different samples of fuller's earth for methylene blue is no criterion of its capacity to catalyse the decomposition of hydrogen peroxide. The adsorptive powers were in the ratios of 2.54, 2.18 and 1. The catalytic actions were in the ratios 2.38, 0.58 and 2.51. The iron content of the three earths is possibly the governing factor in the catalysis.

Adsorption and the Influence of Support Materials

Palladium, spread on active charcoal, with the object of utilising the adsorptive capacity of the support material in addition to the catalytic activity of the metal has been employed by Foster and Brude[3] in a study of carbon monoxide decomposition to yield carbon and carbon dioxide at temperatures as low as 100°C. Hydrogen had no influence on the change. The reaction went even with the smallest amounts of water vapor present which points to direct reaction

$$2CO = CO_2 + C$$

With silica gel as support material this reaction was accompanied by the reaction

$$CO + H_2O = CO_2 + H_2$$

since hydrogen was present in the effluent gas. This work is in disagreement with previous claims of Orloff[4] who stated that hydrogen and carbon monoxide yield ethylene in presence of nickel-palladium catalysts. Foster and Brude obtained no unsaturated compounds and state that it is safe to assume that ethylene has not as yet been produced by reduction of carbon monoxide. There should be some information forthcoming from American sources on this point.

Rosenmund and Langer[5] have shown that the nature of the support material is of importance in protecting the catalyst against poisons as well as in influencing the catalytic activity. With palladium catalysts on various supports the influence of arsenious oxide and carbon monoxide as poisons was studied, in the reduction of cinnamic acid. Kieselguhr-palladium catalysts showed the least activity and greatest sensitivity to poisons. Blood charcoal gave the most active and most resistant preparations. In these two cases activity and resistance run parallel. Barium sulphate supports are more active than pumice; the latter are more active in presence of the poisons.

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[1] See Freundlich: "Kapillarchemie," p. 182 (1922).
[2] J. Chem. Soc., **121**, 2119 (1922).
[3] Ber., **56**, 2245 (1923).
[4] Ber., **42**, 893 (1909).
[5] Ber., **56**, 2262 (1923).

The effect of the supports is evidently a function of the adsorptive capacity of the support for the poison. It acts in these cases as a purification agent in the catalyst system.

Adsorption by support materials has proved to be of importance in the measurement of adsorption by contact catalysts spread on supports. Dr. R. A. Beebe has shown that asbestos suitable for use as support for platinum in contact mass catalysts adsorbs 0.79, 0.10 and 0.04 cc. nitrogen and 53.0, 11.3 and 2.0 cc. sulphur dioxide per gram at 0°, 110° and 218°C respectively. Russell, in Princeton, has shown that pumice used as a support for nickel adsorbs 1.2 cc. nitrogen per gram at 110°C. This possibility has always to be looked for in adsorption studies.

Heats of Adsorption

Benton's paper previously cited indicates the existence of primary and secondary adsorptions the former, only, of which parallels the catalytic activity. The thermal magnitudes accompanying such adsorptions should reveal if any extensive change in the valence forces has occurred during such adsorption. It is for this reason that particular interest attaches to the measurements of heat of adsorption which are now being made.

Foresti[1] has measured the heat of adsorption of hydrogen on nickel and showed that the heat of adsorption, Qv, at atmospheric pressure was 11500+500 calories. Beebe and Taylor[2] have shown by direct measurement that the heats of adsorption of hydrogen on active catalysts composed of nickel and of copper are respectively about 13500 and 9600 calories. The great disparity between these values and that of the heat of liquefaction of hydrogen, 450 calories, is the first striking feature of these results. The adsorption is very definitely not a simple condensation process. Taken in conjunction with the variation of adsorption with pressure, as elucidated by the work of Gauger and Taylor and of Pease, the heats of adsorption may be utilised to demonstrate the difficulty of formation of multi-molecular films of such gases. From the equation

$$\text{Log}\ \frac{p_2}{p_1} = \frac{\lambda}{4.57}\ \frac{T_2-T_1}{T_2T_1}$$

calculation may be made of the pressure p_2 at which, at temperature T_2, the same weight of gas may be adsorbed as is taken up by the adsorbent at T_1 at a pressure p_1, the heat of adsorption being λ. The data of Gauger and Taylor show that at 25°C and 40 mm. pressure a given sample of nickel adsorbed 8.7 ccs. of hydrogen. Utilising the directly observed value for λ = 13500 cals., we may now calculate with the aid of the above equation the pressures at which this quantity of gas will be adsorbed at various higher temperatures.

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[1] Gazz. chim. ital., 53, 487 (1923).

[2] J. Am. Chem. Soc., 46, 43 (1924).

Temperature	Calculated Pressure at which 8.7 cc. H_2 are adsorbed
80°C	1.85 atm.
184°C	95 atm.
218°C	414 atm.
305°C	3342 atm.

The experimental measurements show, however, that, for example, at 184°C., as much as 8.0 ccs. of gas are already adsorbed at 150 mm. pressure. It is therefore evident that a further increase in pressure from 150mm. to 95 atmospheres only results in the further adsorption of 0.7 ccs. This result is in entire agreement with that found experimentally, that the adsorption between 150 mm. and 760 mm. at 184°C., was, within the error of measurement, constant. The calculated variation should be $\frac{0.7}{95}$ = somewhat less than 0.008 ccs. Similar considerations hold to a more marked degree at the higher temperatures. At 305°C and 1 atm. pressure the adsorption is already some 5.5 ccs. The adsorption of an additional 3.2 ccs. would require a gas pressure of 3342 atmospheres.

In a similar manner utilising the heat of adsorption of hydrogen on copper, $\lambda = 9600$ cals., it may be calculated that the quantity adsorbed at 0°C and 1 atmosphere would be adsorbed at 110°C at 162 atmospheres. Now, actual test has shown that at 110°C and 1 atm., pressure the adsorption of hydrogen by an active copper is already 87 per cent. of that at 0°C and 1 atmosphere. An increase in hydrogen pressure of 161 atmospheres would only result therefore in an increase of $\frac{13 \times 100}{87} = 15$ per cent. in the adsorbed gas.

We regard the slight variation of adsorption with pressure after the initial strong adsorption at the lower partial pressures in the cases herein studied as the strongest evidence in favor of the Langmuir theory of a unimolecular layer. There is evidently in these cases little or no tendency to build up several layers of adsorbed molecules on such surfaces.

There is evident a similar inability to build up several layers of adsorbed gas in the case of carbon monoxide on copper as first observed by Jones and Taylor[1] and recently more thoroughly investigated by Pease.[2] The same is apparently true for the cases of hydrogen and carbon monoxide on platinum as the recent studies of Pollard[3] show. In all these cases there is evident rapid saturation of the surface at low partial pressures and then subsequent slight increase of adsorption with pressure. The available data on heats of adsorption for these latter cases confirm this view. Mond, Ramsay and Shields[4] value for the heat of adsorption of hydrogen is 13760 cals. Langmuir[5] has calculated by an indirect method that the heat of adsorption of carbon monox-

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[1] Colloid Symposium Monograph, p. 108 (1923).

[2] J. Am. Chem. Soc., **45**, 2296 (1923).

[3] J. Phys. Chem., **27**, 365 (1923).

[4] Z. physik Chem., **25**, 657 (1898).

[5] Trans. Faraday Soc., **17**, 641 (1921).

ide on platinum is 32,000 cals. The heats of adsorption of oxygen and chlorine on charcoal are known to be high[1], and charcoal is an oxidation and halogenation catalyst.

One other feature of these data on heats of adsorption other than the actual magnitudes involved is of importance. Beebe's measurements of the variation of heat of adsorption with pressure, over the range 0-760 mm., show the magnitude to be constant. This is in sharp contrast to the results previously obtained with adsorbents of the charcoal type. In this latter case the heat of adsorption decreases steadily with increasing pressure, the final values approaching those of the heat of liquefaction of the adsorbed gas. This has been interpreted as showing that the adsorption is really a liquefaction phenomenon, the excess heat, over and above that of liquefaction, being accounted for by the high compression supposed to obtain in the first liquid layers of adsorbed gas, such pressure diminishing as more and more layers form, until, finally, the straight heat of condensation is obtained. The constancy of the values obtained in our studies and their wide divergence from the heat of liquefaction (13500 and 9600 calories as compared with 450 calories heat of liquefaction) tends to indicate that in the cases we have studied no multimolecular layers form.

It is interesting to note that, from Pease's data on ethylene, a gas whose isotherm at 0°C. on copper is much more reminiscent of isotherms on charcoal, the value for the heat of adsorption deduced from the isosteres at 0°C., and 20°C. (5.5 ccs. adsorbed at 480 and 760 mm. respectively) may be calculated to be 3750 calories, which is exactly what would be deduced from Trouton's rule. From the isosteres at lower pressures, higher heats of adsorption are calculable. From the isosteres for 3.85 ccs. (200 and 300 mm. respectively) the calculated value is 5100 calories. This is in accord with previous data on non-specific or capillary adsorption. Much of our evidence tends to show that ethylene may be adsorbed in capillaries in some of our copper samples. With other samples, notably one obtained in Princeton recently where the adsorption of ethylene at one atmosphere pressure was only one-half that of the hydrogen adsorption[2], capillary adsorption seems to be less evident. We incline to the belief that the high initial values of heats of adsorption should be ascribed to the heat of the adsorption complex, adsorbent-adsorbate, for example, $Cu\text{-}C_2H_4$; with capillary liquefaction, the heat measured becomes more and more that of the liquefaction, $C_2H_4\text{-}C_2H_4$. Under such circumstances the variation of the heat of adsorption with pressure would provide a definite criterion of the formation of multi-molecular adsorbed gas films.

Interface Phenomena

Further evidence of interface phenomena[3] in chemical reactions is revealed by reaction velocity curves autocatalytic in nature. Sieverts and Theberath[4] studied the dissociation of silver permanganate and obtained such a reaction

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[1] Unpublished work. M.I.T.
[2] See also Pease: loc cit..
[3] Cf. Second Report, J. Phys. Chem., 27, 827 (1923).
[4] Z. physik. Chem., 100, 463 (1922).

process. Small amounts of impurities increased the velocity of decomposition. Hinshelwood[1] thereupon promptly called Sieverts attention to his own work upon both inorganic compounds and explosives such as tetryl in which an auto-accelerated change occurs. It is not quite clear whether Hinshelwood accepts the interface theory as accounting for his experimental results. "Now since the rate of reaction in the solid state is only about 50 to 100 times less than that in the liquid (in the case of tetryl at 120°C) we must assume that even after the most careful purification the tetryl still contains traces of impurity which either give rise to liquid or exert some catalytic effect." Is it not possible that these "traces of impurity" may simply be weak spots in the tetryl crystal lattice, from which reaction starts and spreads outwards.

Otto and Fry[2] thought that their results showed the decomposition of potassium chlorate to be a unimolecular process. Anyone can see that they are in reality a beautiful example of an autoaccelerated process. Iron oxide promotes the decomposition. Recently they have shown that potassium chloride does the same thing.[3] The presumptionis the refore strong that the process is an interface phenomenon. Neville has added[4] to this reaction an interesting case of promoter action. Impure pyrolusite was more effective than pure manganese dioxide. The pyrolusite contained 8 per cent. iron oxide. A mixture of 8 per cent. iron oxide and 92 per cent. pure manganese dioxide had the same efficiency as the impure pyrolusite. The action of the mixture was more than additive of the effects of the two oxides separately; hence the promoter action, elucidation of the mechanism of which was not achieved. It will probably be quite complex.

Jones and Taylor[5] have shown that the low temperature reduction of copper oxide by carbon monoxide is an interface phenomenon, inhibited by carbon dioxide and by oxygen. The catalysis of the carbon monoxide and oxygen reaction by copper oxide appears to be alternate oxidation and reduction. On copper the process is oxidation of adsorbed carbon monoxide. In this factor it differs markedly from the catalysis of hydrogen and oxygen on copper, the mechanism of which appears to be alternate oxidation and reduction.

Gas-Liquid Reaction Velocities and Catalysis

Norrish and Rideal[6] have recently studied the reaction,

$$H_2 + S\ (\text{liq.}) \text{ --- } H_2S.$$

They emphasise that the solubility of hydrogen sulphide in liquid sulphur may have vitiated the earlier work performed by means of a static method, since the gas would be liberated on solidification of the sulphur and would therefore be added to the equilibrium quantity of hydrogen sulphide measured after cooling the reaction bulbs. Furthermore, Norrish and Rideal point

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[1] Phil. Mag., 40, 569 (1920); Proc. Roy. Soc., 99A, 203 (1921); J. Chem. Soc., 118, 721 (1921).

[2] J. Am. Chem. Soc., 45, 1134 (1923).

[3] J. Am. Chem. Soc., 46, 269 (1924).

[4] J. Am. Chem. Soc., 45, 2330 (1923).

[5] J. Phys. Chem., 27, 623 (1923).

[6] J. Chem. Soc., 123, 696 (1922).

out, it is uncertain whether in the earlier work the walls of the vessel acted catalytically; also, the abnormal temperature coefficient obtained by Bodenstein, 1.34, between 234° and 283°C and 1.77 between 310° and 356°C does not seem to be in harmony with Bodenstein's conclusion that the reaction is homogeneous and confined to the gas phase.

Norrish and Rideal, by employing a dynamic method, have found it possible to show that the combination of hydrogen and sulphur takes place by way of two reactions, a gaseous and a surface reaction, the former being predominant, under the conditions of their experiments at 285°C., and upwards, the latter being the more important below this temperature. They showed also that the temperature coefficients of the two separate reactions were constant but widely different in value.

These conclusions were reached by an analysis of the reaction velocity measurements. These revealed that the logarithms of the total reaction velocity plotted against temperature did not yield straight lines. The curves obtained confirmed Bodenstein's result of an increasing temperature coefficient with increasing temperature. From measurements at different temperatures with two different hydrogen pressures, p_1 and p_2, it was found that a plot of the logarithms of the differences of corresponding velocities for the two pressures against temperature gave a straight line. This fact led the authors to the conclusion that a surface reaction and a gas reaction were proceeding concurrently and that the former, assumed independent of the gas pressure and therefore constant, disappeared on taking the difference of the corresponding velocities. In other words, the straight line obtained as stated is in reality the graph of the gas reaction velocity occurring at pressure p_1-p_2. Assuming that the gas reaction velocity was proportional to the pressure and the surface reaction independent of the gas pressure, the observed curve for total reaction was resolved into two straight line curves of logarithm of velocity plotted against temperature for the two reactions taken separately. From the slope of these lines the temperature coefficients were obtained. That for the surface reaction was found to be 1.48, that for the gaseous reaction was 2.26 which after correcting for the variation of the vapor pressure of sulphur with the temperature reduced to 2.19. Corresponding to these coefficients, by applying the Arrhenius equation,

$$\frac{d \log V}{dT} = \frac{A}{RT^2}$$

where V is the reaction velocity, the values of A, the heats of activation of the gaseous and surface reactions, were found to be respectively 52400 and 26200 calories. Norrish and Rideal call especial attention to the fact that these are in the ratio 2:1.

By varying the size of the reaction vessel they showed also that the surface reaction was directly proportional to the internal surface area of the vessel and independent of the quantity of sulphur in the bulb. The respective reaction equations would therefore be:—

$$V\ (\text{gas}) = k_1 \times C_{H_2} \times C_S$$

$$V\ (\text{surface}) = k_2 \times \text{Surface area},$$

where C_{H_2} refers to the hydrogen concentration, C_S that of the monatomic sulphur.

Norrish and Rideal[1] showed also that oxygen functions catalytically in the union of hydrogen and liquid sulphur. The phenomenon is in reality quite complex. With rise of temperature and increase of oxygen concentration beyond 10 per cent. at a temperature of 265°C., and beyond 7 per cent. at 285°C., the catalytic action becomes a poisoning action. The observed effects were separated into a strong poisoning effect in the gaseous reaction between hydrogen and sulphur at all temperatures and a catalytic effect on the surface reaction which only becomes observable at the lower temperatures (265 and 285°C.) where the surface reaction is of greater relative importance. This surface catalytic action rises to a maximum with increase of oxygen concentration in the hydrogen and then falls away again, finally becoming a poisoning action for concentrations of oxygen beyond 10 per cent. Simultaneously, sulphur dioxide is formed at a rate directly proportional to the oxygen concentration.

From the known velocities of the several reactions occurring, it was deduced that the effects observed may be quantitatively explained by postulating a gradual preferential adsorption of oxygen by the sulphur surface, all the hydrogen being displaced when the gaseous concentration of oxygen has exceeded 10 per cent, and by ascribing to the oxygen a catalytic activity proportional to the number of molecules adsorbed per square centimetre of surface. From these assumptions Norrish and Rideal calculate the composition of the adsorbed gas films in equilibrium with a given atmosphere. It is evident from this work and that of Pease[2], that experimental determinations of such adsorptions would be instructive.

In a concluding section of the paper Norrish and Rideal consider the mechanism of both gaseous and surface reactions. The thermal value found from the temperature coefficient of the gaseous reaction, the "critical increment" of the radiation theory, 52400 cals., is in agreement with Budde's value[3] for the heat of dissociation of S_2 molecules into atoms, and thus corresponds to the energy required to sever two sulphur bonds. The critical increment of the surface reaction similarly corresponds to the breaking of one sulphur bond and is equal to that required to sublime a molecule of S_2 from the surface, which also involves the breaking of one bond. The surface reaction is considered to take place in two stages: (1) adsorption of the molecule involving the breaking of one bond and (2) removal of the molecule of hydrogen sulphide involving breaking of the second bond, the critical increment measured corresponding to the slower of the two processes. The authors also assume that the surface contains mainly S_8 molecules of which a few are opened by the rupture of a linkage and thus polarised. The adsorption of the hydrogen and the oxygen is assumed to occur at these positions. The catalytic effect of the oxygen is attributed to simultaneous adsorption of oxygen and

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[1] J. Chem. Soc., 123, 1689 (1923).

[2] *loc cit.*

[3] Z. anorg. Chem., 58, 169 (1912).

hydrogen at the two ends of the ruptured S_8 molecule. The strong attracton of the oxygen for the sulphur at one end of the chain will cause a weakening of the force by which the sulphur is held at the other end and thus lower the critical increment of energy necessary to remove the end sulphur atom as hydrogen sulphide.

Rideal and Norrish[1] show the union of liquid sulphur and oxygen to occur at the liquid surface and also on the walls of the containing vessel, and to proceed as well on the latter as on the former, pointing to the existence of a liquid film covering the whole surface of the vessel. The reaction is proportional to the oxygen pressure; the temperature coefficient is 1.63 composite of two reactions with coefficients respectively 1.48 (A) and 1.77 (B). The reaction A is independent of pressure beyond 0.41 atm. The reaction B is proportional to the oxygen pressure as far as 1 atm. pressure. The critical increment of A is 25750 cals. (cf. preceding); that of B is 37450 cals. Two types of sulphur molecules are presumed to be present in the surface layer giving rise to the A and B reactions.

Inhibition Phenomena

Sieverts and Lueg[2] have investigated the effect of various poisons on the rate of solution of metals in acids. Alkaloids such as nicotine, cocaine, cinchonine were effective, naphthoquinolines, strychnine, brucine, narcotine and quinine were very effective. The extract consisting of the ether soluble basic constituents of crude anthracene was most effective. For slight amounts of poison, temperature increase reduces the inhibition; for large amounts it is without effect. No obvious connection between inhibition and increase in overvoltage could be found. The authors consider that adsorption of the poison on the metal surface accounts for the inhibition which is expressible by an empirical equation $\frac{Ko-Kc}{Kc}=aC^b$ where Ko is the uninhibited velocity, Kc that with poison concentration c; a and b are constants.

Simultaneous Action of Catalysts and Radiation

Rosenmund, Luxat and Tiedemann[3] have investigated the influence of ultra-violet light on the reactivity of halogen ring compounds in presence and absence of catalysts. From the preparative standpoint an indication of their results may be gleaned from the results in the following case, the reaction between brom-benzol and sodium iso-amylate dissolved in isoamyl alcohol.

12 hours heating, with copper, without radiation	5.2%	Halogen as NaBr
12 hours heating, without copper, with radiation	34.8%	" " "
12 hours heating, with copper and radiation	76.9%	" " "

Sodium bromide and the corresponding ether were produced, the temperature being the boiling point of the solution.

Comparison measurements of the velocity constants were made: (1) with copper alone; (2) with ultra-violet light alone; and (3) with both agencies, in the case of reaction between *p* brom-benzene sulphonic acid and potassium

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[1] J. Chem. Soc., 123, 3202 (1923).
[2] Z. anorg. Chem., 126, 193 (1923).
[3] Ber., 56, 1950 (1923).

hydroxide solution, under the chosen conditions and at as low a temperature as possible. They showed that (1) was extremely slow, (2) was much faster, and (3) was at least twice as great as would be calculated from addition of (1) and (2). The explanation of (2), the acceleration by light alone, is to be attributed to the action of the light in activating the halogen compound. For (3) several possible explanations can be given

(a) Radiation activates the catalyst

(b) The molecule activated by radiation offers more favorable working conditions to the catalyst. This assumption is favored by Rosenmund and co-workers. They had previously shown a more powerful influence of copper in thermal reaction when the stability of the halogen in the molecule had been reduced somewhat.

They investigated a number of compounds in which the stability of the halogen in the compound increased until they found in *p* chlor-benzoic acid a substance of which the chlorine is held so fast that under the given working conditions, (t = 104°C) copper alone was inactive. In this case the velocity when radiated was the same with or without copper. They therefore conclude that the radiation does not influence the copper.

Schwarz[1] thought that Röntgen rays activated contact platinum in the contact process, and in the decomposition of hydrogen peroxide. More recently, Schwarz and Klingenfuss[2] attribute the greater efficiency of the platinum to a photolysis of the water present giving rise to a more active form of oxygen, probably in the form of a peroxide of platinum.

The suggestion of Ellinger[3] that the increased activity was to be attributed to the taking up of electrons by the metal from the radiation, thereby facilitating oxidation processes, is rejected by Schwarz who points out that this should hold true equally well whether water were present or absent. The presence of water was shown to be necessary.

Poisons

The elucidation of the mechanism of the action of poisons may result in a further contribution to the problem of mechanism in contact catalysis itself. Some beginnings of great significance are already evident. Armstrong and Hilditch pointed out some years ago[4] that "the amount of toxic material necessary for total suppression of catalytic activity is far below that required for stoichiometrical combination with even the surface layers of the catalyst. The probability that an 'active catalyst' is merely an average term expressing a surface on which a number of patches of maximum activity occur (the greater part of the surface being of quite a low order of activity) offers a simple explanation of the discrepancy, selective adsorption of the catalyst poison at the relatively few points of maximum activity causing the disappearance of practically all catalytic effect."

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[1] Ber., 55, 1040 (1922).

[2] Z. Elektrochem., 29, 470 (1923).

[3] Z. physiol. Chem., 123, 257 (1922).

[4] Faraday Society Symposium, Discussion 17, 670 (1922).

This point of view seems to be capable of experimental verification and the results of Pease, already cited (loc. cit) are the beginnings of quantitative exploration of this idea. Pease showed that an amount of mercury which reduced the adsorptive capacity of hydrogen to 1/20th of its value before poisoning and which reduced the adsorption of ethylene but little, brought about a reduction in velocity to 1/200th of its value before poisoning. A little consideration will show that this is in good agreement with Armstrong and Hilditch's conclusion.

Pease is now extending this quantitative study to the determination of the action of carbon monoxide on the combination of ethylene and hydrogen in presence of copper. His results to date demonstrate that the carbon monoxide molecules required to suppress the reaction, under the conditions of the experiment, are markedly less than the number of hydrogen molecules capable of being adsorbed by the copper catalyst. This seems to be quantitative evidence that only a fraction even of the surface which is capable of adsorbing hydrogen is capable of accelerating the reaction.

It will be noted that this idea is in agreement with conclusions from other investigations on the adsorption of catalytic agents, notably those of Benton previously discussed, on primary and secondary adsorptions of carbon monoxide on oxide catalysts and the parallelism between the catalytic efficiency and primary adsorption data. The conclusion suggests that attention should be concentrated on adsorptions at low partial pressures and on the heats of adsorption at these pressures. This complicates the experimental problem involved but it seems to be a necessary complication.

Co-actions and the Mechanism of Reduction

Prins[1] has contributed a suggestive paper on the mechanism of reduction and of oxidation reactions when a third substance is present in addition to the essential reactants.

"Oxidation reactions. Lead peroxide and manganese peroxide are insoluble in weak acids, but react easily if a third component is present which can co-operate in the attack on the peroxide, by reacting with the surplus of oxygen." Such a substance may be an aldehyde or any other easily oxidisable compound. For the same reason an acid which, moreover, can function as an aldehyde, like formic acid, dissolves these peroxides easily: other examples are acids with one or more OH groups, CO groups etc.

On the same principle, a weak but easily oxidised acid can supplant a much stronger one if, under the circumstances the latter contains active oxygen.

Thus the nitrates, chlorates, etc., of the heavy metals are converted into formates by the action of formic acid: the simplest method of preparing nickel formate consists in adding a saturated solution of nickel nitrate to about 85 per cent formic acid, which is heated on a water bath. A violent reaction takes place with evolution of carbon dioxide and nitric oxide and the resulting nickel formate separates nearly quantitatively.

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[1] Rec. Trav. chim., 42, 473 (1923).

Reduction reactions. The co-action of three components is of special importance in the reduction of organic substances with a metal and an acid, or with a ferro-, stanno- salt etc., which takes the place of the metal in the reduction.

It is a well-known fact that metals which are practically insoluble in a certain acid, become markedly so if this acid co-acts with an oxidising substance, but in most cases the course of the reaction is uncertain.

It is often supposed, that the oxidising agent first forms an oxide and this reaction is succeeded by a reaction between oxide and acid.

But from the fact that compounds like nitrobenzene act just as powerfully without being able to form an oxide, it is certain that the primary formation of an oxide is not a necessary phase in the reaction.

Moreover, the action of an oxidising agent is often selective, which can be shown even with test tube experiments: e.g. silverfoil is only slowly soluble in a mixture of an inorganic acid and hydrogen peroxide, much quicker in a mixture of the same acids and potassium bichromate but it dissolves almost immediately in a mixture of potassium permanganate and even a weak organic acid, such as acetic acid.

This is not caused solely by the instability of the oxidising agent, because neither the unstable hydrogen peroxide, nor the unstable perchromic acid have the same influence; it is, obviously, not caused therefore by oxygen in statu nascendi. If this were true, hydrogen peroxide would react most powerfully. In order to study the co-action in cases where the primary formation of a metal oxide was excluded, we chose some years ago[1], the co-action between a metal, an acid and reducible organic substances such as nitrobenzene and benzaldehyde.

Nitrobenzene accelerates in some cases more than a thousandfold. In these cases it was necessary to expose the metal in the other flasks long after that in the nitrobenzene solution had totally vanished in order to get a weighable loss.

In some instances, benzaldehyde shows the same property, although in a lesser degree, whereas in other cases benzaldehyde causes a decided decrease in the velocity of reaction.

This retardation, is probably due to adsorption either of the benzaldehyde or of its reduction products, whereby part of the surface of the metal becomes inactive.

An acceleration of about the same order of magnitude takes place in a non-ionizing medium like parafin-oil or in one in which the ionisation is very small.

Consider the reaction between the metal and the acid. It is usually supposed that the metal forms positive metal-ions in the liquid, the hydrogen ions taking up the liberated electrons to form a hydrogen atom or molecule.

The difference in strength of the acids is usually expressed as the magnitude of the ionisation under comparable circumstances, but the cause of this difference must be sought in the chemical character of the anion. It is, there-

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[1] H. J. Prins: Proc. Akad. Wetensch. Amsterdam, 23, 9 (1921).

fore, to be expected that the anion plays an important part in the reaction between an acid and a metal; their difference in behavior cannot be explained by the concentration of the hydrogen ions, because the latter is, in its turn, a function of the acid radicle, which retains the electron and expels the hydrogen ion.

If we consider the case from the purely chemical viewpoint, we have to account for the different results obtainable with different combinations of metal and acid and for the obvious co-action between the three components. This may be done as shown by Prins,[1] by considering the reciprocal changes of the equilibrium between atomic and link-energy caused by the collision of two molecules.

The oxygen atom and the metal atom coming within their mutual sphere of action lose potential energy, which is partially taken up by the chain $O{=}C{-}O{-}H$, causing a disturbance of the equilibrium between atomic and link energy, which finally causes an increase in the atomic energy of the hydrogen atom. An analogous activation occurs in the chain of metal atoms on the surface of the metal. In this way an activation is reached by asymmetric complex formation. If the compound is split up by taking up energy (for example through collision with a third molecule), the components leave the compound in a state of increased activity.[2]

The initial reaction is caused by the affinity between the unsaturated oxygen atom and the metal and the phenomenon will be a purely chemical one in a non-ionising medium[3]. If at the same time a reducible compound is present, the reaction proceeds further: the reducible compound takes up the activated hydrogen and a metallic salt is formed. As opposed to this the action of an acid upon a metal in an ionising medium consists in the discharging of a hydrogen ion by the metal, a reaction which is probably hampered by the adsorption of the undissociated molecule upon the metal.

The fact that the reduction can take place with the non-ionized molecules explains the fact that even in 80 per cent acetic acid, the reduction reaction can attain enormous velocities, notwithstanding the small concentration of the hydrogen ions. The reduction reaction is then a polymolecular reaction with at least three components: acid, metal and reducible substance.

An acceleration in the hydrogen evolution between for example zinc and 80.3 per cent acetic acid is only caused by phenyl hydroxylamine in the presence of nitrobenzene, if the concentration of the latter is small. A piece of zinc, after etching with dilute hydrochloric acid gives a marked evolution of hydrogen in acetic acid 80.3 per cent at 52°. This evolution stops immediately if so much nitrobenzene is added that the solution becomes 0.75 molar. A molar solution of phenylhydroxylamine does not stop the evolution, but

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[1] Chem. Weekblad 14, 68 (1917).

[2] H. J. Prins: Rec. Trav. chim. 42, 25 (1923).

[3] The same activation takes place with other oxygen containing substances e.g. nitrobenzene, ketones, aldehydes and the effect upon the hydrogen evolution depends upon the velocity with which the substance is reduced in connection with the magnitude of the adsorption. In accordance with this view with more negative metals like sodium the activation of the metal is not the last stage of the reactions with active oxygen containing substances, but proceeds till a metal atom is extracted from the surface.

if so much nitrobenzene is then added, that the solution becomes 0.75 molar with regard to nitrobenzene, the evolution of hydrogen stops again immediately; if these substances are added in the reverse order the result remains the same. Aniline in molar concentration has no appreciable influence upon the hydrogen evolution.[1]

From this we may conclude: 1. that the hydrogen ion if it is adsorbed upon the surface of the zinc, can be supplanted by the nitrobenzene or its immediate reduction product, if the nitrobenzene is present in a sufficient amount. 2. that the nitrobenzene molecules or their immediate reduction products either cover the surface totally or cannot be supplanted by the phenylhydroxylamine molecules. 3. aniline is not adsorbed to an appreciable extent.

It is therefore probable that nitrobenzene is strongly adsorbed and rapidly reduced, phenylhydroxylamine less strongly adsorbed and aniline practically not at all, the cause of this must be sought in the diminishing chemical activity of the characteristic groups NO_2, NHOH, NH_2 towards zinc, thus exhibiting the close relationship between adsorption and chemical reaction The adsorption obviously turns the oxygen atom towards the zinc; with removal of the oxygen atom the adsorption vanishes.

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[1] The action of phenylhydroxylamine may be demonstrated as follows: Etched zinc is heated in a test tube with about 80 per cent. acetic acid to boiling, then the tube is cooled till the hydrogen evolution becomes imperceptible, addition of a small quantity of phenyl hydroxylamine directly causes a marked hydrogen evolution. In an analogous way the action of nitrobenzene may be demonstrated.

INDUCED OXIDATION AND THE EXPLANATION OF THE INTERNAL USE OF IRON SALTS AND OF FEVER

BY N. R. DHAR

Since the days of Lavoisier, the phenomenon of slow oxidation has attracted numerous workers, especially because the great biological phenomenon of life mainly depends on slow oxidation.

The immortal chemist Lavoisier was the first to apply the balance and the thermometer to the investigation of the phenomenon of life and he declared in 1780 "La vie est une fonction chimique." The work of today is but the continuation of that done a century and more ago. Lavoisier and Laplace made experiments on animal heat and respiration. Lavoisier declared that life processes were those of oxidation with the resulting elimination of heat. The fundamental fact that the quantity of oxygen absorbed and of carbon dioxide given out depends primarily on (1) food (2) work and (3) temperature, was established by Lavoisier within a few years after his discovery that oxygen supported combustion. Writing in 1849 Regnault and Reiset remarked "Les recherches modernes ont confirmé ces vues profondes de l'illustre savant." It was however, quickly noted that if carbon and hydrogen burn in the lungs, the greatest heat would be developed there, a result not in accordance with observation. It was then suggested that the blood dissolves oxygen and that the production of carbon dioxide and water took place through oxidation within the blood. Through the critical studies of Liebig which were published in 1842, it was observed that it was not carbon and hydrogen which burn in the body, but protein, carbohydrates and fat; it was also proved that the amount of oxygen needed in metabolism depends upon the chemical composition of the material that burns in the organism.

Rübner showed that if the diet were increased from a medium to an abundant supply the metabolism as indicated by the heat production increases.

The fact that food materials, not affected by molecular oxygen at ordinary temperatures, are oxidised with the greatest ease within the animal body into their end-products is a really wonderful phenomenon. One can at once realise how remarkable this is by reflecting upon the intense heat required to burn completely a bit of protein upon a platinum foil, although it is extremely easy for the body to break down a large quantity of protein.

Traube seems to have been the first to adopt the idea of an oxidising ferment and to give expression to the happy idea that there occur in the body readily oxidisable substances which have the power of transferring the oxygen in the active form to substances which are oxidisable with difficulty, such as the food materials.

We have been successful in imitating these biological processes in the laboratory. In studying induced reations we have found out that substances like starch, cane sugar, etc., which are not directly oxidised at ordinary temperatures by atmospheric oxygen, can be oxidised by the same agent when they are mixed with substances like sodium sulphite or freshly precipitated ferrous hydroxide which themselves undergo oxidation in air. Thus, oxidation has been induced[1] in the following substances in presence of Na_2SO_3 or freshly precipitated $Fe(OH)_2$: urea, starch, grape sugar, cane sugar, $K_2C_2O_4$, CH_3-COONa, sodium potassium tartrate, sodium formate, sodium citrate, acetone, chloral hydrate, chloroform, glycerol, quinine sulphate, sodium succinate, methyl alcohol, ethyl alcohol, phenol, glutaric acid, maltose, potassium stearate, cholesterol, anthraquinone, acetanilide, brucine, phenolphthalein, gum arabic, etc.

The wide application of these induced reations is evident from the fact that these various compounds which do not undergo oxidation by atmospheric oxygen under ordinary conditions can be readily oxidised when mixed with Na_2SO_3 or freshly precipitated $Fe(OH)_2$ which is itself being oxidised. It is evident that there will be different stages of oxidation of these organic compounds until the final products of oxidation are obtained. It is impossible to ignore the importance of these reactions in their relation to the phenomenon of oxidation and reduction in the animal body. It is well known that a molecule of stearic acid taken into the body in the form of fat undergoes combustion so that eventually each of its 18 carbon atoms will become converted into carbon dioxide. But no one imagines that such a change is immediate or direct, or that every carbon atom simultaneously parts with its attached H-atoms and by combining with oxygen yields CO_2 and H_2O. We have brought about the same change in the laboratory with potassium stearate by inducing its oxidation through the oxidation of Na_2SO_3 or $Fe(OH)_2$ by passing oxygen through the mixture at the ordinary temperature. In the animal body, acetic acid is oxidised with great ease into CO_2 and H_2O, though it is resistant to strong oxidising agents such as chromic acid, potassium permanganate, etc. Its oxidation in the laboratory has been effected by us with the help of sodium sulphite or ferrous hydroxide when it is being oxidised by passing oxygen through it. Oxalic acid although very readily oxidised by many laboratory reagents is oxidised with great difficulty in the animal body; we have also observed that oxalic acid is only very slowly oxidised by passing air through a solution of oxalic acid or an oxalate containing a sulphite. The substances undergoing active metabolism in the animal body, comprising the proteins, carbohydrates, fats, and their derivatives are practically resistant to oxidation by oxygen under ordinary conditions. Yet in the animal body the carbon of these compounds is readily oxidised to carbon dioxide. It is generally conceded that the same process of activation of the atmospheric oxygen must take place in the body in order to account for the observed chemical changes. It is remarkable that a very large number of biochemical oxidations have been imitated by us in the laboratory by the simple process of induced oxidation as already mentioned.

It has been shown in a previous paper that the oxidising power of hydrogen peroxide at the ordinary temperature is greatly accelerated in presence of ferrous and ferric salts.[2] Thus, if tartaric acid or starch or sugar and hydrogen

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[1] Compare Dhar: Proc. Akad. Wetensch. Amsterdam, 33, 1074 (1921); Mittra and Dhar; Z. anorg. Chem. 122, 146 (1922).

[2] Dhar: J. Chem. Soc. 111, 697 (1917).

peroxide be brought together at the ordinary temperature, hardly any chemical reaction takes place; but, as soon as a ferrous or ferric salt is added, oxidation of tartaric acid or starch takes place rapidly. Reactions of this type are of great importance in explaining the oxidation in the human body. The food in the animal body is oxidised by the atmospheric oxygen, giving us heat and energy. In the animal body there is evidence with regard to the formation of the peroxide from the oxygen taken up by the animal and this peroxide oxidises the food taken up in the body. We have shown in the laboratory that the activity of H_2O_2 at the ordinary temperatures is accelerated markedly by the presence of ferrous or ferric salts. Similarly, in the animal body, iron in the haemoglobin present in the blood accelerates catalytically the oxidation of the food stuff by the peroxide formed in the body from the inhaled oxygen. When there is a deficiency of iron in the blood, the animal body suffers from anaemia because the amount of catalyst necessary for regular oxidation falls short. At this stage any iron salt taken into the system will supply the natural deficiency and the necessary amount of oxidation will take place. This is the probable mechanism of the internal use of iron salts, whether ferrous or ferric, in medicine.

Curiously enough oxalic acid is only slightly oxidised by hydrogen peroxide aided by a ferrous or a ferric salt, although it is readily oxidised by many laboratory reagents; in the animal body oxalic acid is oxidised with great difficulty.

Iron in some form or other is essential to the life of many, perhaps, all forms of protoplasm. In the vertebrates this is obscured by the fact that most of the iron is contained in the haemoglobin of the blood, and its importance in other tissues is generally ignored. In the invertebrates, however, in many of which no corresponding compound exists in the blood, considerable amounts of iron are found in the tissues and there is no question but that, throughout the animal kingdom, iron is essential to living matter. It has been proved that it is also necessary for the development of lower vegetable forms and it has been found that in its absence the higher plants fail to form chlorophyll. The presence of iron plays an important part in the oxidation reactions in plants and animals.

Iron has been long used in the treatment of anaemia more especially of the form known as chlorosis and it was tacitly assumed that it was readily absorbed from the alimentary tract and was utilised by the tissues to form haemoglobin. Nothing is definitely known regarding the changes which the preparations undergo in the stomach and in the intestines or the form in which the iron is absorbed. I am of the opinion that at least a part of the iron added to the system is taken up in the haemoglobin. If the iron is administered in the ferrous state, it passes into the ferric condition in the body and usually exists as a part of a complex radical and in a colloidal condition. This complex, by coming in contact with the peroxide formed from the inhaled oxygen, forms a higher oxide of iron which oxidises food materials. In medicine almost any ferrous or ferric salt, preferably of weak acids or as part of a complex ion, can be used, because the mechanism will be nearly the same in all cases.

There is another important factor which should not be lost sight of. In the foregoing pages, it has been observed that the oxidation of substances like Na_2SO_3 or $Fe(OH)_2$ can induce the oxidation of materials like fats, proteins, sugars, starch, etc. It seems probable, therefore, that in the animal body there exists readily oxidisable substances, which may be enzymes containing traces of ferrous or manganous radicles in complex colloidal condition; and the oxidation of these substances induces the oxidation of food materials.

I shall now try to discuss the phenomenon of fever from the point of view of catalytic chemistry. By fever is generally understood a complex of phenomena, the dominant characteristic of which is a rise of body temperature. In a foregoing paper[1] it has been proved that, in general, increase of temperature increases the metabolism in the animal body if determinations are made under standard conditions. It has also been observed in that paper that temperature has a very marked effect on the killing of toxins and bacteria by antitoxins and antiseptics. This marked influence of temperature is extremely useful for men and animals. When a toxin enters the system, the temperature of the body usually rises by two or three degrees and we get the phenomenon of fever and the poison is destroyed about 10 or 20 times more quickly at this fever temperature. Why is this rise of temperature? I am inclined to the view that the phenomena of fever is really an autocatalytic reaction. It is well known that the body heat is obtained by the oxidation of food stuffs by the atmospheric oxygen which is inhaled. In the foregoing pages, it has been said that the amount of heat generated in unit time, depends on the nature of the food material taken and it also depends on the velocity of the oxidation of the food material. I am of the opinion that when a poison enters the body it secretes a fluid which acts as a positive catalyst in the oxidation of foodstuffs by the inhaled oxygen. For example when a malarial parasite enters the body, either the parasite itself or its secretion, which is taken up by the blood, acts as a positive catalyst in the oxidation of the food material by the oxygen of the blood. In other words, the speed of oxidation becomes greater in presence of the parasites or their secretions and hence the amount of heat generated per unit time becomes greater and we get the phenomenon of fever. If no external food material is used, the fats and proteins in the body will be consumed and that is why a person suffering from fever becomes thin and loses weight. It has already been said that when the body temperature rises, the amount of oxidation, like all other chemical changes, becomes greater with the increase of temperature and that is the reason why I call fever an autocatalytic chemical change in the animal body. Apparently there are two causes of increased oxidation in the phenomenon of fever. One is the catalytic acceleration of oxidation of food materials due to the presence of parasites or their secretions and the second is due to the increased temperature of the body which causes an increase in oxidation.

In a discussion of fever one must consider two possible causes: (1) an increase in heat production; and (2) a decrease in the facilities for the discharge of heat produced. It seems to me, from a survey of the literature on fever,

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[1] Dhar: Proc. Akad. Wetensch., 23, 44 (1920).

that physiologists and bio-chemists have no definite opinion about the origin of the rise in temperature. Hence I venture to bring the above suggestion for their consideration.

It is well known that the action of metals on nitric acid becomes more and more rapid as the chemical change progresses; because the chemical change is largely accelerated by nitrous acid which is a product of the change. Similarly the action of formic acid on iodic acid or nitric acid is an auto-catalytic change. To my mind fever resembles these auto-catalytic changes.

Summary and Conclusions

1. The oxidation of sodium sulphite or of ferrous hydroxide by air or oxygen can induce the oxidation of substances like fats, proteins, sugar, starch, etc., at the ordinary temperature.

2. It is likely that in the animal body there exist readily oxidizable substances, which may be enzymes containing traces of ferrous or manganous radicles in complex colloidal condition and the oxidation of these substances induces the oxidation of food materials.

3. The oxidizing power of hydrogen peroxide on starch, sugar, tartaric acid, etc., is greatly accelerated by traces of ferrous or ferric salts at the ordinary temperature.

Similarly in the animal body, the iron in the blood accelerates catalytically the oxidation of food stuffs by the peroxide formed in the body from the inhaled oxygen. When there is a deficiency of iron in the blood, the animal becomes anaemic. At this stage any iron salt taken in the body will supply the natural deficiency and the necessary amount of oxidation will take place.

4. It is suggested that fever is an auto-catalytic reaction. The oxidation of substances like starch, sugar, proteins, etc. by oxygen in the animal body is believed to be catalytically accelerated by parasites or secretions of bacteria. Hence the amount of heat generated in the animal body per unit time is increased and the phenomenon of fever is observed. Moreover, like all other chemical changes, the amount of oxidation in the animal body per unit time is also increased by the incipient rise of temperature.

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NEGATIVE AND POSITIVE CATALYSIS AND THE ACTIVATION OF MOLECULES

BY N. R. DHAR

In 1811 Kirchhoff observed that mineral acids converted starch into dextrine and sugar, but that the acids themselves did not undergo any change.

More than a century ago Döbereiner showed that spongy platinum caused hydrogen to ignite in contact with air. Since then many facts have been added in the domain of catalysis, and industrial developments have been made; but hardly any substantial light has been thrown on the mechanism of catalytic reactions in general. In the following pages an attempt has been made to explain the mechanism and to unify catalytic phenomena (positive and negative) from considerations based on the formation of intermediate compounds. The importance of recent work of physicists on radiationless transfer of energy in the problem of activation of molecules and atoms and in catalysis in general, has also been emphasised.

Negative Catalysis

In the foregoing papers[1] the subject of negative catalysis has been investigated and a mechanism of negative catalysis in several oxidation reactions has been suggested based on intermediate compound formation. The following lines of argument were advanced in those papers. The same considerations can be extended to several other cases of negative catalysis.

It is well known that a solution of sodium arsenite is not oxidised by atmospheric oxygen under ordinary conditions. On the other hand, a solution of sodium sulphite is readily oxidised to sodium sulphate. If we mix the two together and expose the mixture to air or oxygen, the oxidations of arsenite and of sulphite go on simultaneously. At the same time a curious phenomenon takes place—the velocity of the oxidation of sodium sulphite becomes very small in presence of sodium arsenite. In other words, sodium arsenite which is undergoing a slow oxidation acts as a powerful negative catalyst in the oxidation of sodium sulphite. Similarly the solution of an oxalate which also undergoes slow oxidation in presence of sodium sulphite, which is itself being oxidised, slows down to a marked extent the oxidation of sodium sulphite by atmospheric oxygen, moreover we have observed that manganous hydroxide, ferrous hydroxide and sodium thiosulphate which are slowly oxidised by passing oxygen in presence of a solution of sodium sulphite retard markedly the oxidation of sodium sulphite. Also ferrous salts retard the oxidation of stannous salts in air. It appears probable, therefore, that the phenomenon of negative catalysis in oxidation reactions is possible only when the catalyst is liable to be oxidised. I have observed that manganous salts act as powerful

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[1] Dhar: J. Chem. Soc. **111**, 707 (1917); Proc. Akad. Wetensch. **23**, 1074 (1921); Dhar and Mittra: Trans. Faraday Soc. **14**, 1, 17 (1922).

negative catalysts in the oxidation of formic and phosphorous acids by chromic acid, and manganous salts easily pass into the manganic state. Moreover it has been shown by various investigators that organic substances, notably quinol, brucine, sugars and other reducing agents, act as negative catalysts in the oxidation of sodium sulphite by oxygen. It is well known that the oxidation of phosphorus by oxygen or air is retarded by the vapours of various organic substances e.g. ether, alcohol, turpentine, etc., and that the oxidation of chloroform is retarded by the presence of a small quantity of alcohol.

According to Moureu and Dufraisse[1] a trace of quinol can suppress the oxidation of benzaldehyde. Moreover Lifschitz and Kalberer[2] have shown that ether retards the slow oxidation of various magnesium alkylhalides of the Grignard type, which oxidation is revealed by luminescence on exposure of the substance to air. Similar retardation has been observed by Delépine[3] in the oxidation of organic sulphur compounds by air.

Now all these negative catalysts are good reducing agents and are themselves readily oxidised. Hence in oxidation reactions, the phenomenon of negative catalysis takes place when the catalyst itself is liable to be readily oxidised.

Schönbein first noticed that when certain substances are undergoing oxidation spontaneously by atmospheric oxygen, one part of the oxygen combines directly with the substance undergoing oxidation—whilst another part of it, is either converted into ozone or hydrogen peroxide, or oxidises some other substances simultaneously. Schönbein demonstrated still further that just so much oxygen is rendered active as is consumed by the substance which is being oxidised; or, in all slow oxidations, the same amount of oxygen is required as is consumed in the formation of hydrogen peroxide from water or is consumed in the induced oxidation. Later investigators like Jorissen, Engler and Wild have verified the law of Schönbein in several cases. If we expose a mixture of sodium sulphite and arsenite to atmospheric oxygen, according to Schonbein, one atom of oxygen should go to oxidise sodium sulphite, while the other oxygen atom would oxidise a molecule of sodium arsenite in the same time. The oxidation of sodium arsenite is a very slow chemical change and in order that Schönbein's law be applicable it follows immediately that the oxidation of sodium sulphite, which is fairly rapid should become a slow change and the velocity of this oxidation should become equal to that of the oxidation of sodium arsenite by oxygen, because the same amount of oxygen will be taken up by the reducing agent at the same time. As a matter of fact, from our experiments, we find that in presence of sodium arsenite or potassium oxalate, or ferrous hydroxide or manganous hydroxide, the velocity of oxidation of sodium sulphite by air becomes very small. We assume that a molecule of oxygen splits up in this reaction into two atoms and each atom oxidizes one of the reducing agents. Now as a solution of sodium sulphite is much more readily oxidized than a solution of sodium arsenite, it becomes difficult

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[1] Compt. rend. 174, 258; 175, 127 (1922).
[2] Z. physik. Chem. 102, 393 (1922).
[3] Bull. 31, 762 (1922).

to understand why the other oxygen atom instead of attacking the readily oxidizable unattacked sodium sulphite, prefers to react with the much more difficultly oxidized sodium arsenite. Or if we assume that at first a peroxide of the type of Bödlander's benzoyl peroxide is formed as a combination of the sodium sulphite with a molecule of oxygen, we are still encountered with the same difficulty. In this case we shall have to assume that this peroxide, instead of attacking the readily oxidizable sodium sulphite, will react with the less readily oxidizable sodium arsenite by preference. It seems, therefore, that the only course left to us is to find out the explanation in the theory of the formation of a complex of sulphite and arsenite or of sulphite and oxalate, this complex being oxidized as a whole. It is well known that complex sulphites and oxalates do exist. I have observed in a previous paper[1] that, in the oxidation of sulphites and sulphurous acid, the sulphite ion is the active agent. If we decrease the concentration of the sulphite ion we can decrease the rate of the chemical change, and a solution of H_2SO_3, which is a weak acid containing few SO_3'' ions, is oxidised less readily than a solution of sodium sulphite of the same concentration. On the addition of an arsenite to a sulphite a complex which itself is oxidized as a whole is formed, at the same time the velocity of oxidation of sulphite becomes less due to the decrease in the concentration of the sulphite ions arising out of the formation of a complex of arsenite and sulphite or of SO_3'' and an oxalate. Hence it seems that the only plausible explanation of negative catalysis in oxidation reactions stands on the theory of formation of unstable, intermediate compounds of the catalyst and one of the reacting substances. These views[2] were advanced more than three years ago. In a recent paper Taylor[3] has come to similar conclusions with regard to the retarding influence of water on the decomposition of oxalic acid by concentrated sulphuric acid, decomposition of diazoacetic ester, etc. Consequently the consensus of opinion at the present moment is in favour of the view that intermediate compounds are formed in the phenomenon of negative catalysis.

From considerations based on chemical dynamics Ostwald criticised adversely the conception of intermediate compound formation in the explanation of catalytic phenomena. He advanced the argument that in order to explain positive catalysis by the theory of intermediate compound formation, it was necessary to show that the intermediate reactions actually took place more readily than the direct reaction under the given conditions; because if a reaction proceeded more slowly through an intermediate product than the direct path, it would take the latter and the possibility of intermediate products could have no influence on the process. "Hence" added Ostwald[4] "I see no possibility of explaining retarding catalytic influences by the intermediate products."

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[1] Dhar: Versl. Akad. Wetensch. 29, 479 (1920).

[2] Dhar: Proc. Akad. Wetensch. 1921, 23, 1074 (1921).

[3] J. Phys. Chem. 27, 322 (1923).

[4] Nature, 65, 522 (1902).

My arguments in favour of the view of intermediate compound formation as an explanation of negative catalysis have already been put forth and they are certainly based on considerations of the velocity of chemical changes involved.

In a foregoing paper[1] it has been proved that the oxidation of sodium formate by iodine is a bimolecular reaction and the change takes place according to the following equation $HCOONa + I_2 = HI + NaI + CO_2$. The iodine is dissolved in potassium iodide. The reaction is retarded by iodide ions and hence there is a slight lowering of the velocity coefficient as the reaction proceeds, due to the continued increase in the concentration of the iodide ions which are products of the reaction. One peculiar point has been observed namely, that, if there is a definite concentration of potassium iodide, the velocity coefficient does not depend on the concentration of iodine, but the velocity coefficient falls off if we start with a definite concentration of iodine and increase the concentration of KI.

This effect cannot be explained from the mass action equilibrium $KI + I_2 \rightleftarrows KI_3$. When we use 1.27 grams of iodine and 5.4132 grams of KI we get k_1 at 25° = 0.00196 and when we use 0.635 grams of iodine and 2.7066 grs of KI, k_1 becomes 0.00379. The concentrations of sodium formate in these two cases are equal and according to the mass action equilibrium the velocity coefficient should be the same.

Similarly the oxidation of sodium formate by $HgCl_2$ is retarded by chloride ions. From the experimental results it has been observed that in this case also the velocity coefficient was independent of the concentration of $HgCl_2$. If however, the effect of the chloride be simply to form a complex with mercuric chloride, $HgCl_2 + RCl = RHgCl_3$ the velocity coefficient would naturally depend on the concentration of $HgCl_2$. The oxidation of potassium oxalate by iodine is also retarded by iodide ions. Similarly the oxidation of potassium oxalate by $HgCl_2$ is retarded by chloride ions.

All these oxidation reactions are retarded by hydrogen ions, because in these oxidations the formate and oxalate ions are taking part. Similarly we have proved that in the oxidation of sodium sulphite by air, the sulphite ions are active.

These cases of negative catalysis are similar to those on the influence of HBr on the hydrolysis of bromosuccinic acid studied by Müller[2] and on the hydrolysis of several organic halogen acids studied by Senter and Porter[3].

Temperature Coefficients of Catalysed and Non-catalysed Reactions

From my researches on the temperature coefficients of thermal and photochemical reactions the following general results have already been established:

1. A positive catalyst diminishes and a negative catalyst increases, the temperature coefficient of a reaction, the decrease or increase being the greater, the higher the concentration of the catalyst.

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[1] Dhar: J. Chem. Soc., 111, 707 (1917).

[2] Z. physik. Chem. 41, 483 (1902).

[3] J. Chem. Soc. 99, 1049 (1910).

2. When light acts as an accelerator, the temperature coefficient of a reaction carried on in light is smaller than that of the reaction in the dark.

3. Reactions which are very sensitive to the influence of temperature are also sensitive to the influence of light.

4. The simpler the order of a reaction, the greater is its temperature coefficient. In other words, uni-and bi-molecular reactions have higher temperature coefficients than multimolecular ones.

Physiological processes mostly take place in heterogeneous medium. The Brownian movement of the colloidal particles present in the reacting substances does away with the diffusion layer characteristic of heterogeneous reactions, and makes the physiological processes similar to positively catalysed reactions taking place in homogeneous medium. Consequently the temperature coefficients of physiological processes, instead of being small (about 1.2) are generally greater than 2 for a 10° rise.

In calculating the temperature coefficient of a reaction the Arrhenius formula $\log k_1/k_2 = A(T_1-T_2)/T_1T_2$ is applied. Consequently the value of a temperature coefficient for a 10° rise becomes smaller as the temperature rises. Experimental results on the determination of temperature coefficients of chemical reactions have always supported the conclusion that the temperature coefficient becomes smaller as the temperature rises. Consequently, in all my work on the temperature coefficients of catalysed and uncatalysed reactions comparisons of temperature coefficients have been made between the same temperature interval.

On page 332 of Taylor's paper (loc. cit) the following occurs in connection with the temperature coefficient of the action of strong sulphuric acid in presence of a trace of water; "Therefore the temperature coefficient of the whole decomposition process should diminish with increase of water content in the solution. This is actually the case. The higher value, 4.42, of the temperature coefficient is for a dilution of 0.1% water in the interval 25°-35° C. At 70°-80° C for a 3% water concentration, the temperature coefficient of 3.35 is obtained." I have already said that the temperature coefficient of a chemical change falls off as the temperature rises. If we calculate according to the Arrhenius formula, the temperature coefficient between the interval 70°-80° C with 0.1% water concentration in the decomposition of oxalic acid by sulphuric acid, we get a value 3.08 which is less than that obtained with 3% water concentration between 70°-80° C (3.35). Hence the conclusion of Taylor is erroneous. These results of Bredig and Lichty can be readily explained on our theory that a negative catalyst increases the temperature coefficient of a reaction. Water is a negative catalyst in the above reaction and the greater the concentration of water the greater is the retardation and consequent increase in the temperature coefficient.

Consequently in presence of 3% water the temperature coefficient of the reaction between oxalic acid and sulphuric acid should be higher than that with 0.10 water. The results of Bredig and Lichty are in agreement with our general conclusions already cited.

There is a difficulty with regard to the action of sulphuric acid on oxalic acid; the reaction is represented as $H_2C_2O_4+H_2SO_4=H_2O+CO+CO_2+H_2SO_4$. Bredig and Lichty have shown that the chemical change follows the unimolecular formula. The negative catalyst, water, is being formed continually as a product of the chemical change; consequently the unimolecular coefficients, instead of remaining constant, should decrease as the change proceeds. Similarly Meyer's work[1] on the reaction between formic acid and sulphuric acid show that an unimolecular coefficient is obtained, although the negative catalyst water is being continually formed in the system. Experimental work is in progress in these laboratories to settle these points and other cases of positive and negative catalysis.

Some comment should be made on accepted views about the temperature coefficients of photochemical reactions. Hitherto the opinion has been generally held that in light the temperature coefficient of photochemical reactions should be about unity. On the contrary my researches prove that the temperature coefficient of a reaction occurring in light may have any value but it will be smaller than that of the reaction in the dark if light accelerates the change. The diminution of temperature coefficient depends on the acceleration of the reaction in light[2].

It is well known that if light of definite wave-lengths falls on metals like Na, K, Cs, etc., electrons are given out at ordinary temperatures. The photoelectric emission of electrons is hardly affected by increase of temperature. On the other hand thermoionic emission is greatly increased by increase of temperature. Ordinarily, chemical reactions carried on in the dark are expected to obey the same laws as govern the emission of electrons from heated substances, whilst ideal photochemical changes should follow the same laws as are applicable to photoelectric emission. In reality, ideal photochemical reactions are very rare and that is why the temperature coefficients of many photochemical reactions are usually greater than unity.

Positive Catalysis and its Mechanism and the Activation of Substances

In many cases of positive catalysis consistent explanations can be given of the phenomena if we assume that intermediate compounds are formed. Let us take the decomposition of potassium chlorate by heat in presence of MnO_2 and other manganese salts. If ordinary $KClO_3$ is heated till it melts and is allowed to cool the solid usually shows a light pink colour. The reason of the pink colour is this:—the chlorate ordinarily is obtained from chlorine prepared by the Weldon method and the chlorine thus prepared carries with it a little manganous salt. Hence the potassium chlorate is contaminated with a little manganous salt. If the potassium chlorate is fused the manganous salt is changed into permanganate by oxidation with potassium chlorate and hence the pink colour. Several years ago McLeod[3] threw out the suggestion that possibly potassium permanganate would be an intermediate stage in the decomposition of $KClO_3$ in presence of MnO_2 by heat, but he could not actually obtain

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[1] Z. Elektrochem. 15, 506 (1909).

[2] Dhar. J. Chem. Soc. 123, 1856 (1923).

[3] J. Chem. Soc. 55, 184 (1889).

any permanganate by using $KClO_3$ and MnO_2. By utilising $MnSO_4$ instead of MnO_2 as a catalyst we have been able to obtain $KMnO_4$ directly as an intermediate substance in the decomposition of $KClO_3$ in presence of manganese salt. Quantitative experiments are in progress in this laboratory, which show that appreciable quantities of $MnSO_4$ are converted into $KMnO_4$ when $MnSO_4$ is added to $KClO_3$ which has just melted. $KClO_3$ does not begin to decompose till it attains the temperature of about 450° C whilst $KMnO_4$ decomposes at about 250°C. Consequently the ready decomposition of $KClO_3$ when it is just melted in presence of MnO_2 or manganous salts is readily explained. The intermediate product $KMnO_4$ which is formed decomposes at the melting temperature of $KClO_3$.

It is well known that in the chamber process of the manufacture of H_2SO_4, the SO_2 is oxidized very readily by nitrogen peroxide which is obtained by the action of oxygen on nitric oxide. In this as well as in the previous cases, the activation of the chemical changes involved can be readily explained on the theory of the formation of intermediate substances which favour the chemical changes. The velocity of oxidation of SO_2 by molecular oxygen is small whilst through the intervention of nitric oxide which in its turn becomes converted into nitrogen peroxide, the speed of the oxidation of the SO_2 is increased.

In the contact method of H_2SO_4 manufacture the speed is increased by spongy platinum, platinised asbestos, platinum black, or any other substance of this type.

What is the mechanism of this activation? If we can assume that the catalyst platinum black converts a molecule of oxygen into oxygen atoms, then the mechanism would have been clear, because an atom of oxygen is certainly more active than a molecule of the same substance. When a molecule is converted into atoms it takes up energy. Thus about 80000 calories of heat are necessary to atomise a molecule of hydrogen. What is the origin of this energy? If the adsorption of oxygen by platinum black could take up heat, then we could have imagined that the amount of heat taken up would be utilized in the formation of oxygen atoms, but as a matter of fact when gases are adsorbed by substances like platinum, charcoal, palladium, etc., heat is given out instead of being absorbed. From the researches of Favre,[1] Mond, Ramsay and Shields[2] and others we know that large quantities of heat are given out when NH_3 is adsorbed by charcoal or hydrogen by palladium, platinum, etc. Hence we cannot imagine that hydrogen is converted into the atomic state when it is adsorbed by palladium or that the oxygen is converted in the atomic state, when adsorbed by platinum black. Very recently, however, Richards and Richards[3] have suggested that hydrogen occluded in iron is in the atomic condition.[4]

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[1] Ann. Chim. Phys. (3) 37, 465 (1853).

[2] Proc. Roy. Soc. 62, 50, 290 (1897).

[3] J. Am. Chem. Soc. 46, 89 (1924).

[4] Compare Langmuir: Ibid. 34, 1310 (1912).

In explaining hydrogenation reactions, Sabatier and others, assume that with metals like nickel, hydrogen forms an unstable hydride like NiH_2 or Ni_2H_2 and that this hydride is capable of giving out atomic hydrogen which is more active than the molecular variety[1]. Very recently, Schlenk and Weichselfelder[2] have brought further evidence in support of the view that NiH_2 is formed in these hydrogenations.

If we pass hydrogen through a solution of $FeCl_3$ we find that the ferric chloride is not reduced to the ferrous state, but if we add a little palladium foil to the solution it will convert the ferric salt to the ferrous state. Similarly oxygen adsorbed by platinum black is more active than molecular oxygen and can readily oxidize ethyl alcohol, formic acid, oxalic acid, etc.

How are these molecules activated? How can the adsorption process activate these molecules? Our knowledge about metallic hydrides has increased considerably during the last few years.[3]. Recently Peters[4] has proved that hydride of lithium, can be electrolysed in the fused condition, hydrogen being evolved at the anode and the metal at the opposite electrode. We can imagine that when H_2 is passed over finely divided nickel or through palladium, an unstable hydride is formed and this hydride decomposes into the metal and hydrogen in the atomic or in an active condition, which is capable of inducing the process of hydrogenation involved. Unfortunately there is no direct experimental evidence in support of this view. In order to avoid this difficulty, Bancroft[5] explains these cases on the view of increased concentration of one or more of the reacting substances at the surface of the catalyst due to adsorption. He explains most cases of contact catalysis in heterogeneous systems on this increase of concentration.

Let us take the case of the reaction between SO_2 and oxygen again. Instead of ordinary catalysts, light may be utilized in activating the oxygen molecules. We have observed that if SO_2 and O_2 are exposed in glass vessels to tropical sunlight, crystals of SO_3 are obtained at the ordinary temperature. We can imagine that the sunlight has activated the oxygen molecules, which have reacted with the sulphur dioxide at the ordinary temperature. It is difficult to state at this stage whether the light converted the oxygen molecules into an active form or into atoms[6]

In this connection the recent work of physicists on radiationless transfer of energy would be interesting. The experiments on ionisation potential first carried out by Franck[7] and his colleagues are now well known. They deal with interchange of energy between freely moving electrons and atoms. A stream of electrons moving with a definite velocity is projected into a mass of gaseous matter. When an electron happens to pass close to an atom, then,

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[1] Sabatier: "La Catalyse en Chimie organique", 60 (1920).

[2] Ber. 56B, 2230 (1923).

[3] Compare Jaubert: Compt. rend. 142, 788 (1906); Moers: Z. anorg. Chem. 113, 179 (1920) and others.

[4] Z. anorg. Chem. 131, 140 (1924).

[5] J. Phys. Chem. 21, 571 (1917).

[6] Compare the work of Wendt, Landauer and Ewing: J. Am. Chem. Soc. 44, 2377 (1922) on the activation of chlorine by light.

[7] Ber. physik. Ges. 15, 34, 373, 929 (1913); 16, 457 (1914).

provided the energy of the free electron exceeds a certain limit, the whole of its energy may be transferred to the valency electrons lying at the outer periphery of the atom. The valency electron is therefore uplifted to higher quantum orbits. This state is not stable and in a short time reverts to its original position, the excess of energy being set free as monochromatic radiation. Thus the atoms take away energy from the free electrons and convert it into its own energy of monochromatic radiation. When the energy of the bombarding electron is sufficiently large it may tear off the valency electron from the parent atom. This stage is known as "ionisation". Hitherto the attention of all workers has been confined to only one side of the problem, namely communication of energy from the free electron to the atom. But Klein and Rosselund[1] showed that the reverse process, namely communication of energy by an excited atom to a free electron actually takes place in many cases, e.g. a mass of mercury atoms, some of which have been activated either by absorption of light $\lambda = 2536$, or by the electric discharge. If an electron passes close to it the mercury atom may transfer its energy ($\lambda = 2536$) to the electron. The electron thus receives an increment in its velocity but the transfer is radiationless. The electron chokes the emission of light $\lambda = 2536$. These observations further extended by Franck and his students[2] who showed that the excited atoms may communicate their energy not only to the electron but also to such atoms and molecules which may come into their contact. These atoms or molecules will therefore receive either some increment in their kinetic energy or if the energy imparted be sufficiently large they may be excited to their spectral emission, ionisation or dissociation in the case of molecules. These ideas therefore open out a very promising field of investigation. For example, Franck activated a stream of mercury vapour by light $\lambda = 2536$ and these activated mercury atoms were allowed to act upon hydrogen gas. It was proved that gaseous hydrogen was converted into a atomic state even at a temperature of about 40°. This atomic hydrogen was capable of converting cupric oxide into the cuprous state at such a low temperature as 40°, at which temperature molecular hydrogen cannot reduce cupric oxide. The explanation is that when a mercury atom absorbs light $\lambda = 2536$ it is loaded with an energy content of 4.9 volts. On coming in contact with hydrogen molecules which are thereby broken into atoms as the heat of dissociation of hydrogen is about 80000 calories which corresponds to 3.8 volts.

It seems from these results that the active nitrogen of Lord Rayleigh[3] ozone, active hydrogen, active chlorine, etc. may be supposed to be really activated nitrogen, activated oxygen, activated hydrogen, activated chlorine, from the point of view of Franck. When a moderately condensed electric discharge is sent through nitrogen gas, the latter is converted into an excited state falling short of dissociation into its constitution atoms. According to this view, active nitrogen is probably excited nitrogen molecule loaded with a certain voltage. Its great activity is due to the ease with which these active

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[1] Z. Physik, **41**, 46 (1921).

[2] Z. j. Physik. **9**, 259 (1922); **11**, 161; **17**, 202 (1923).

[3] Strutt: Proc. Roy. Soc. **85A** 219 (1910); **86A**, 56, 262 (1911); **87**, 179 (1912).

molecules give out this extra amount of energy. We all know that ozone is formed by passing a silent electric discharge through oxygen, we can therefore imagine that the so-called substance ozone is nothing but oxygen in an excited condition and charged to a certain voltage. It is well known that ultra-violet light can convert oxygen into ozone. Recently Weiser[1] and his colleagues and Downey[2] have proved that the glow of phosphorus in oxygen gives out ultra-violet light and that this ultra violet light converts no oxygen into ozone. From the point of view of Franck we know that mercury vapour can be excited by electric discharge as well as by light of $\lambda = 2536$.

Consequently we can imagine that oxygen is also activated and is charged to a certain voltage by silent electric discharge or by ultra-violet light. Similarly the active forms of gases like hydrogen, chlorine etc., prepared by Wendt[3] and colleagues, Venkataramaiah[4], and others[5] are probably activated molecules of these gases, charged to be a certain voltage. Their activity is due to the readiness with which they can give out this extra amount of energy and hence can induce many chemical changes which these gases in molecular condition cannot effect. It is well known that when silent electric discharge is passed through oxygen, there is a contraction in volume. Hence it appears that the active form of oxygen occupies less space than molecular oxygen. Similar contraction in volume has been observed by Venkataramaiah[6] when silent electric discharge is passed through chlorine. It is impossible to say whether active nitrogen occupies less space than molecular nitrogen because Lord Rayleigh has not studied this question. Since in the case of activation of oxygen or chlorine, there is a contraction in volume, it is probable that in the formation of active nitrogen there will also be a contraction in volume. Lord Rayleigh has shown that active nitrogen gives a glow. It is probable that this glow is due to the reversion of the active variety into the inactive molecular form.

In this connection, it will be interesting to consider the phenomenon of phosphoresence from these points of view. For example when calcium sulphide is exposed to light, it absorbs light energy and becomes converted into an active form and is charged to a certain potential. In the dark, this activated calcium sulphide would pass into the inactive form and would give out light. It is needless to point out that the active condition of matter is certainly an unstable state of affairs and its natural tendency will be to revert to the stable inactive form. There is a striking analogy between the after-glow of active nitrogen and the phenomenon of phosphorescence ordinarily observed. Lord Rayleigh,[7] Tiede and Domcke,[8] Pirani[9] and others have shown that abso-

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[1] J. Phys. Chem. **25**, 61, 349, 473 (1921).

[2] J. Chem. Soc. **125**, 347 (1924).

[3] J. Am. Chem. Soc. **42**, 930 (1920).

[4] J. Phys. Chem. **27**, 74 (1923).

[5] Compare Lowry: J. Chem. Soc. **101**, 1152 (1912); Koenig and Elöd: Ber. **47**, 516 (1914).

[6] Loc. cit.; also Nature: **106**, 46 (1920).

[7] Loc. cit.; also Proc. Roy Soc. **91A**, 303 (1915).

[8] Ber. **47**, 2283 (1914).

[9] Chem. Zentr. **1921 I**, 200.

lutely pure nitrogen does not give an after-glow. Traces of H_2S, oxygen, SO_2 etc., are necessary for obtaining an appreciable after-glow. Similarly it is well known that the phenomenon of phosphorscence is also associated with traces of impurities in the phosphorescent substances. It seems therefore that there is some similarity between the after-glow of active nitrogen and the phosphorescence of ordinary substances. Similarly we can imagine that emanations from radioactive substances can activate molecules of barium platinocyanide or zinc sulphide and these activated molecules become phosphorescent when they revert to the inactive variety.

The glow due to the slow oxidation of phosphorus has attracted the attention of numerous workers. Recently luminescence has also been observed in the slow oxidation of magnesium alkyl halides[1] and of organic sulphur compounds[2]. It is well known that ions are generated in the slow oxidation of phosphorus and it is very likely that ions would be generated in the other cases of slow oxidations causing luminescence. The ions, in their turn, would convert ordinary oxygen into the activated condition which would readily oxidize substances. Now the conversion of the active form into the inactive variety would cause the luminescence. Recently Downey[3] has shown that the light given out in the oxidation of phosphorus contains short wave lengths and is rich in ultraviolet rays. It will be very interesting to compare the spectrum of this light with that due to the slow oxidations of magnesium alkyl compounds and of organic sulphur compounds. The spectrum of active nitrogen of Strutt has been studied by Fowler and Strutt[4] and it consists of the usual α, β and γ groups of positive bands and contains ultraviolet radiations. I venture to suggest that the ions, given out in the slow oxidation of phosphorus, magnesium alkyl compounds, organic sulphur compounds, etc., would activate the molecular oxygen present there. This activated oxygen would give all the tests attributed to ozone. A part of the activated oxygen without effecting oxidation and hence giving out its extra amount of energy to the oxidizable substance, would spontaneously pass into the inactive variety and would give light rich in ultraviolet rays, which can activate other molecules of oxygen. This is probably the origin of the glow obtained in the slow oxidations of phosphorus, magnesium alkyl halides, organic sulphur compounds etc. I am of opinion that, in these slow oxidations, ions are first produced as products of the chemical change and not due to the glow as suggested by Downey[5].

Very recently Chapman and Davies[6] have shown that when oxygen or hydrogen is driven into fused quartz by the electric discharge, the quartz acquires the property of phosphorescing.

This phenomenon seems to me to be the same as that studied by Lord Rayleigh in connection with active nitrogen. The gas hydrogen or oxygen

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[1] Lifschitz and Kalberer: Loc. cit.

[2] Delépine: Loc. cit.

[3] Loc. cit.

[4] Proc. Roy. Soc. 85A, 377 (1911).

[5] Loc. cit.

[6] Nature, 113, 309 (1924).

adsorbed by quartz becomes active by the electric discharge. The phosphorescence is very likely due to the reversion of the active form into the inactive variety. Lord Rayleigh observed that active nitrogen glowed more intensely at the temperature of liquid air than at the ordinary temperature. Chapman and Davies have also observed that when a small area of the tube is cooled with liquid air while the discharge is passing, that area glows much more brightly than the rest of the tube after the discharge has been stopped.

Consequently like Rayleigh, Chapman and Davies have got active forms of hydrogen and oxygen. It will be interesting to find out whether nitrogen can be activated in this manner. Moreover it is worth while comparing the spectrum of the light given out by oxygen in its phosphorescence by this method and that of the light given out in the slow oxidation of phosphorus, magnesium alkyl compounds, organic sulphur compounds etc. It seems likely that the spectra of the lights given out in all these phenomena would probably be alike, because according to the view advanced in this paper, the glow is supposed to be due in all cases to the transformation of activated oxygen (in one case made energetic by the electric discharge as in the experiments of Chapman and Davies, and in the other cases activation is due to the ions first given out as products of the chemical changes involved) to the inactive molecular oxygen with loss of the extra amount of energy.

It is well known that ions are generated in the oxidation of phosphorus. It is very likely that these ions can activate molecules of oxygen, which thus become reactive and induce chemical changes which are not possible with molecular oxygen. Emission of electrons and ions in many chemical reactions has been observed by Haber and Just[1], Pinkus and de Schulthess,[2] Richardson[3] and others. Moreover, Potter[4] has shown that carbon dioxide liberated during fermentation of glucose through the action of yeast carries both positive and negative ions.

If it can be proved definitely that ions are generated in all slow oxidations, then the phenomenon of induced oxidation will be readily intelligible. For example, let us take the case of the mixture of sodium sulphite and sodium arsenite. If the spontaneous oxidation of sodium sulphite by air or oxygen can generate ions, these ions would activate the molecules or atoms of oxygen, which can then react on the molecules of sodium arsenite.

More over, if it is generally proved that ions are produced in slow chemical changes, a flood of light would be thrown on many complicated induced reactions. In a foregoing paper[5] I have proved that the oxidation of oxalic acid by mercuric chloride is activated by the oxidation of the same substance by permanganate. Thus a solution of oxalic acid is not oxidized by mercuric chloride even in the boiling condition, but if a few drops of potassium permanganate is added to the mixture, the permanganate oxidizes some oxalic acid and at the same time mercuric chloride oxidizes oxalic acid, mercurous chloride

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[1] Ann. Physik. (4) 36, 308 (1911).

[2] J. Chim. phys. 18, 366 (1920); Helv. Chim. Acta, 4, 288 (1921).

[3] Phil. Trans. 222A, 1 (1921).

[4] Proc. Roy. Soc. 91, 465 (1915).

[5] Dhar: J. Chem. Soc. 111, 697 (1917).

coming out as a precipitate. If we can prove that in the reaction between permanganate and oxalic acid, ions are produced and that these ions would activate the molecules of oxalic acid which would reduce mercuric chloride because of its increased energy, then the mechanism of induced reactions of these types would be intelligible.

Moreover, it will be worth while investigating whether ions or electrons are given out when gases like hydrogen or oxygen etc., are adsorbed by platinum, palladium, etc. The ions produced would activate the molecules and would make the chemical change proceed quickly. If this is so, it would explain the catalytic effect of platinum, palladium, nickel in chemical changes.

Summary and Conclusion

(1) Experimental results show that in oxidation reactions, the phenomenon of negative catalysis takes place when the catalyst is liable to be readily oxidized.

(2) The mechanism of negative catalysis in oxidation reactions can be explained on the theory of the formation of intermediate compounds of the catalyst and one or more of the reacting substances.

(3) A positive catalyst diminishes and a negative catalyst increases, the temperature coefficient of a reaction, the decrease or increase being the greater, the higher the concentration of the catalyst.

(4) When light acts as an accelerator, the temperature coefficient of a reaction carried on in light is smaller than that of the reaction in the dark.

(5) The temperature coefficient of photochemical reactions need not be about unity in all cases, but it may be much greater than unity as shown from experimental results.

(6) Thermal reactions carried on in the dark are expected to obey the same laws as govern the emission of electrons from heated substances, whilst ideal photochemical changes should follow the same laws as are applicable to photoelectric emission.

(7) Intermediate compound formation can explain many catalytic accelerations.

It is proved experimentally that potassium permanganate which is more readily decomposed than potassium, chlorate is an intermediate compound in the decomposition of potassium chlorate in presence of MnO_2 and manganous salts by heat.

(8) When gases are absorbed by palladium, platinum, charcoal etc., heat is given out, hence it is difficult to assume that the gases are converted into the atomic state by adsorption.

(9) It is suggested that active nitrogen, ozone, active hydrogen, active chlorine etc., are activated by electric discharge or by light and loaded with a certain voltage. Their great activity is due to the ease with which these activated molecules give out this extra amount of energy.

(10) The glow of active gases like nitrogen, hydrogen, oxygen, etc., the phenomenon of phosphorescence caused by light, the phosphorescence caused by radium emanation, etc., are supposed to be due to the reversion of the activated forms of these substances into the inactive variety with the loss of the extra amount of energy.

(11) All slow oxidations are likely to give out ions and electrons, which could activate the molecules of oxygen. This activated oxygen would give all the tests attributed to ozone. A part of the activated oxygen would spontaneously pass into the inactive variety and would give out light. This is probably the origin of the glow obtained in the slow oxidation of phosphorus, magnesium alkylhalides, organic sulphur compounds, etc.

(12) It seems probable that the ions generated in slow oxidations, could activate molecules of oxygen, which thus become reactive and induce chemical changes which are not possible with molecular oxygen. For example, the spontaneous oxidation of sodium sulphite by air or oxygen can generate ions which would activate oxygen molecules and these active molecules can then react with sodium arsenite. Other induced reactions can be explained in a similar way.

(13) It seems worth while investigating whether ions are given out when gases are adsorbed by Pt, Pd, Ni, etc. If ions are given out during adsorption of gases, this will explain the catalytic effect of these substances.

My thanks are due to Dr. M. N. Saha for his help in writing the paper.

Chemical Laboratory
Muir Central College
Allahabad,
April 30, 1924.

THE WETTING OF BARIUM SULFATE

BY VICTOR LENHER AND H. GORDON TAYLOR

Des Coudres[1] has shown that there are three possible cases when a solid is shaken with two immiscible or partially miscible liquids. This solid may be wetted by one of the liquids to the practical exclusion of the other, in which case it goes into the first liquid. It may be wetted by the second liquid to the practical exclusion of the first, in which case it goes into the second liquid. It may be wetted by both liquids simultaneously, in which case it tends to go into the dineric interface, the surface separating the two liquids. Cases in point with benzene and water are calcium sulfate which goes into the water phase; copper powder which goes into the benzene phase; and calcium carbonate which goes into the interface. Commercial use of this is made in the 'pulping' of white lead when the water is displaced by linseed oil. According to Mr. Euston of the Euston Lead Company, this displacement of the water does not take place rapidly enough for factory work if the acid number is less than four, so the effect is very possibly due more to the free acid than to the oil.

Barium sulfate has been found to give all three types with suitable pairs of liquids. When barium sulfate with a specific gravity of 4.5 is shaken with $SeOCl_2$ (sp.g. 2.44) and the hydrocarbon heptane (sp.g. 0.66), with which selenium oxychloride is immiscible, the barium sulfate settles completely to the bottom, leaving both liquids and the interface clear. Evidently the barium sulfate is wetted completely by the selenium oxychloride. If the barium sulfate is moistened first with heptane, the selenium oxychloride will displace the latter completely.

When a little barium sulfate is shaken with 70% H_2SO_4 (sp.g. 1.6) and selenium oxychloride (these liquids are immiscible and the acid is the upper layer), the barium sulphate is found on top of the interface. Both liquids are left clear and there is not a trace of barium sulfate on the bottom. The reasons for believing that the barium sulfate is on and not in the interface are: firstly, no emulsion is formed; secondly, much more of the solid is supported than would constitute a layer one particle thick in the interface; thirdly, when the tube is given a slight rotary shaking, which causes an eddy current in the liquids without disturbing the level position of the meniscus, the barium sulfate is swept into the upper liquid just as dust is picked up in a whirlwind, while none goes into the lower liquid, which remains clear. The barium sulfate is evidently wetted completely by the upper liquid, 70% H_2SO_4.

When barium sulfate is shaken with heptane and water, the heptane is emulsified in the water, forming globules about as large as bird shot which collect as a deep layer on top of the water. Each globule is coated completely with barium sulphate and the emulsion shows no tendency to crack even on

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[1] Arch. Entwickelungsmechanik, 7, 325 (1898); Hofmann: Z. physik. Chem. 83, 385 (1913); Bancroft: "Applied Colloid Chemistry," 83 (1921).

standing for months. This is similar to the results obtained by Pickering,[1] Schlaefer,[2] Moore,[3] and Sheppard.[4] It sometimes happens that some of the solid stays at the interface while some of it sinks. This may happen in the second case, where the solid is wet by the upper liquid which in this case is 70% H_2SO_4, if the system contains too much $BaSO_4$, or if some of the particles are much larger than the rest. The particles which sink will, however, carry a layer of adsorbed sulphuric acid with them. Some of the solid is more apt to sink, however, in the third case where the solid is held *in* the interface. Here the conditions are more delicately balanced, so that the amount, size, and even shape of the particles may determine whether they will stay in the interface or be pulled down by gravity.

Experiments were made with carbon tetrachloride, heptane, selenium oxychloride, water, sulfuric acid, and phosphoric acid; but no immiscible pair could be found which would float barium sulfate and not strontium sulfate, so a separation of these two salts by this method is impossible as yet. When the sulfates of barium, strontium, and calcium are shaken singly with heptane and water, barium sulfate floats the most satisfactorily and calcium sulfate the least well.

Previous experiments by Lenher have shown that a decidedly gelatinous mass is obtained when precipitated barium sulfate or the ground mineral barytes, is treated with selenium oxychloride. Barium sulfate can be obtained in a gelatinous condition when it is precipitated in selenium oxychloride as a medium instead of in water. If a dilute solution of barium chloride in selenium oxychloride is mixed with a dilute solution of sulfuric acid in selenium oxychloride, barium sulfate is precipitated in a voluminous transparent condition, identical in appearance with a precipitate of alumina. This precipitated gel, as well as the apparently gelatinous mixture of ground barytes and selenium oxychloride, goes over immediately into the pulverulent form when the selenium oxychloride is either removed or destroyed by such substances as water, carbon tetrachloride, sulfuric acid or other reagents.

Studies have been made to determine whether there was any corrosive action of selenium oxychloride on polished surfaces of barite; but no such effect has been detected. Furthermore, careful analysis has shown that the selenium oxychloride does not penetrate the barium sulfate crystals and that selenium oxychloride contains no dissolved barium sulfate even after long standing in contact with it. The evidence therefore seems to be conclusive that the gelatinous barium sulfate obtained by means of selenium oxychloride is merely barium sulfate made plastic or gelatinous by adsorbed selenium oxychloride. This seems to be of distinct importance for the general theory of gelatinous precipitates.

The general results of this investigation are:—

1. Barium sulfate goes into the selenium oxychloride layer when shaken with selenium oxychloride and heptane.

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[1] J. Chem. Soc. 91, 2010 (1907); Kolloid-Z. 7, 14 (1910).
[2] J. Chem. Soc. 113, 522 (1918).
[3] J. Am. Chem. Soc. 41, 940 (1919).
[4] J. Phys. Chem. 23, 634 (1919).

2. Barium sulfate goes into the acid layer when shaken with selenium oxychloride and seventy percent sulfuric acid.

3. Barium sulfate goes into the dineric interface when shaken with heptane and water.

4. The gelatinous barium sulfate obtained by means of selenium oxychloride appears to be barium sulfate made plastic or gelatinous by adsorbed selenium oxychloride.

University of Wisconsin.

REACTIONS IN PHOSGENE SOLUTION. II. FORMATION OF CHLORALUMINATES.*

BY ALBERT F. O. GERMANN AND KENNETH GAGOS

In a recent communication[1] one of us reported that potassium is attacked by phosgene containing dissolved aluminium chloride. The reaction in the case of potassium is too slow for convenient study. The present investigation was undertaken to make a survey of the behavior of other metals towards phosgene containing aluminium chloride, and to find, if possible, examples of the reaction lending themselves more readily to the study of the progress of the reaction.

In the first series of experiments, magnesium, calcium, zinc, cadmium and tin were treated in separate, sealed Faraday tubes with liquid phosgene containing dissolved aluminium chloride. Calcium and magnesium reacted very rapidly, the tube became very hot, and a gas was given off, which, when collected and analyzed, proved to be carbon monoxide. Cadmium, zinc and tin reacted more slowly, in the order named, and all three much more slowly than potassium.

In the case of the magnesium, no solid reaction product separated from the solution; when the solution was cooled in ice, two liquid layers separated, and on further cooling, the denser layer became syrupy. An attempt to study the phase relations of the system soon brought out the fact that more time would be required to complete the study than was available for the investigation; hence the study of this system was abandoned in favor of the system resulting from the action on calcium.

Cadmium, zinc and tin each yielded a solid reaction product, small in amount, forming an incrustation about the metal, and presumably slowing down the reaction. No effort has been made to speed up these reactions by raising the temperature of the system studied, except as mentioned below.

In the case of calcium, the violence of the reaction diminishes after a time; and if the tube be allowed to cool over night, a crystalline product separates, which is neither calcium chloride, because this is entirely insoluble, nor aluminium chloride, since this is very soluble. However, since carbon monoxide is one product of the reaction, it seems reasonable to suppose that calcium chloride is also a product. The crystals, then, are evidently those of a calcium chloraluminate, or a double salt of calcium chloride with aluminium chloride; such a salt was prepared by Baud[2] by fusing the anhydrous salts together.

Before determining this point, it seemed desirable to know the exact function of the aluminium chloride in bringing about the reaction. With this point in mind, the following experiments were performed. Samples of calcium

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* From a thesis presented by Kenneth Gagos in partial fulfilment of the requirements for the degree Master of Arts.

[1] Germann: J. Phys. Chem., 28, 000 (1924).

[2] E. Baud: Ann. chim. phys., (8), 1, 51 (1904).

weighing 0.25 gm. were treated in separate tubes with 10 cc. of liquid phosgene containing varying weighed amounts of aluminium chloride; the reaction was in each case allowed to run to completion, and any residue of calcium was washed with phosgene and weighed. It was thus found that the extent of the reaction is directly proportional to the amount of aluminium chloride present, provided that the calcium and phosgene are in excess.

In other words, the aluminium chloride does not act catalytically in bringing about the reaction; but calcium reacts with phosgene to form calcium chloride, which deposits on the calcium as a protective coating, and arrests further action; when aluminium chloride is present in the solution, it reacts with this surface layer of calcium chloride, forming the soluble double salt, and the reaction proceeds until the free aluminium chloride is exhausted. The same mechanism would apply to magnesium and the other metals.

This interpretation of the reaction is entirely justified by the results of the following experiment, in which magnesium was selected because the product of its reaction with phosgene and aluminium chloride yields a two liquid layer system with phosgene: A gram of anhydrous magnesium chloride was sealed up in a tube with 5 cc. of liquid phosgene and 0.5 gm. of aluminium chloride, and laid aside. When next examined, the magnesium chloride had partly dissolved: cooling the solution brought about separation into two liquid layers, exactly as when metallic magnesium was used. Hence it may be concluded that anhydrous metallic chlorides may react with aluminium chloride in phosgene solution, to form double salts.

Baud[1] isolated one double salt of aluminium chloride with calcium chloride, $1.5CaCl_2.2AlCl_3$; two with barium chloride, $BaCl_2.2AlCl_3$, and $1.5BaCl_2.2AlCl_3$, the second resulting when the first was heated to an elevated temperature, with loss by volatilization of one third of the aluminium chloride. Attempts to prepare $CaCl_2.2AlCl_3$ failed, one third of the aluminium chloride used always subliming, presumably because dissociation takes place at the melting point of the compound, according to the equation:

$$3(CaCl_2.2AlCl_3) \longrightarrow 2\,AlCl_3+2(1.5CaCl_2.2AlCl_3).$$

To determine the formula of the double salt, an excess of calcium was allowed to react with phosgene containing an amount of anhydrous aluminium chloride insufficient to react with all of the calcium as chloride, in a tube provided with a stopcock and stopcock clamp[2]. The reaction, at first violent, became sluggish as the aluminium chloride was used up; the tube, from which carbon monoxide was allowed to escape from time to time, was therefore placed in a boiling water-bath for several hours, or until all action had apparently ceased. On cooling, beautiful amber colored crystals (the color probably due to the presence of iron, which was present as impurity in the aluminium chloride, and doubtless also in the calcium), apparently octahedral, separated. The solution was evaporated to dryness by evacuation, the temperature raised

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[1] Ann. chim. phys. (8) **1**, 51 (1904).

[2] Guye and Drouginine: J. chim. phys., **8**, 503 (1910).

by immersion in a boiling water-bath, and evacuation continued as long as phosgene was evolved. This brought about efflorescence of the crystals, yielding a greyish white powder, which was subjected to analysis.

The results for chlorine are known to be low, as solution of the anhydrous salt was carried out in a covered beaker, and the heat of solution was so great that some hydrogen chloride, resulting from hydrolysis, was lost by volatilization; greater precautions were taken with sample B, but the odor of hydrogen chloride was very evident over the beaker.

	Sample A	*Sample B*
Weight of sample	0.5674 gm.	0.5332 gm.
Weight of silver chloride	1.6495 gm.	1.0747 gm.
Weight of chlorine	0.4081 gm.	0.3896 gm.
% of chlorine	71.92 %	73.06 %
Weight of alumina	0.1641 gm.	0.1536 gm.
Weight of aluminium	0.0873 gm.	0.0814 gm.
% of aluminium	15.39 %	15.27 %
Weight of calcium oxide	0.0834 gm.	0.0781 gm.
Weight of calcium	0.0596 gm.	0.0558 gm.
% of calcium	10.50 %	10.47 %

The formula $CaCl_2.2AlCl_3$ represents this composition very nearly, as is shown in the following comparison:—

	Found A	*Found B*	*Calculated*
Chlorine	71.92 %	73.06 %	74.87 %
Aluminium	15.39 %	15.27 %	14.57 %
Calcium	10.50 %	10.47 %	10.58 %

Iron, present as impurity in the aluminium chloride used, was not determined separately, but appears in the analysis as aluminium. In spite of the precautions taken to ensure complete reaction, aluminium chloride still appears to be present in slight excess.

The calcium salt which Baud was unable to prepare by fusion of the anhydrous salts, has thus been prepared as a phosgenate in phosgene solution. When we attempted to determine the melting point of the dephosgenated salt a portion of the aluminium chloride present sublimed, the salt decomposing according to the equation on page 966, and yielding the compound prepared by Baud.

Composition of the phosgenate. The method used by Baud[1] to determine the composition of the phosgenates of aluminium chloride is unsatisfactory. It was decided instead to determine the pressure concentration diagram at room temperature; the temperature chosen was 19.5°C.

Figure 1 represents diagrammatically the arrangement of apparatus. F_2 is a Faraday tube containing the sample, fastened to the apparatus by means of the universal flat joint and clamp J_2. The tube dips into a thermostat, the

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[1] Compt. rend., 140, 1688 (1905).

temperature of which was maintained at 19.5°C. The manometer M_1, open to the air on one side, communicates with the Faraday tube, and vapor tensions are read on it. A special form of mercury pump[1] of small capacity, P_2, communicates with a second manometer, M_2, and through a P_2O_5 tube and a stopcock, S_{14}, with the system already described. Concentration changes in the solution in the Faraday tube are brought about by withdrawing any desired amount of phosgene vapor from the system by opening the stopcock S_{14} leading to the evacuated mercury pump. The gas drawn off is measured in the gas burette A, communicating with P_2 through the capillary tube V_4, where it is collected by operation of the mercury pump; atmospheric pressure for the reading is attained in the burette by opening stopcock S_{13}, and manipulating the small mercury bulb B_3. After measuring, the phosgene gas is discarded through the operation of a water suction pump, connected to W_3, by opening stopcock S_{12} for a moment. Manometer M_2 serves a double purpose: with the mercury pump entirely evacuated, the barometric pressure is read upon it; and in the withdrawal of a portion of phosgene from the solution in F_2, the amount withdrawn is proportional to the change in pressure as registered on M_2, since volume and temperature are very nearly constant; the change in pressure required to yield 1 cc. of gas when collected in A is determined at the beginning of operations by a direct measurement.

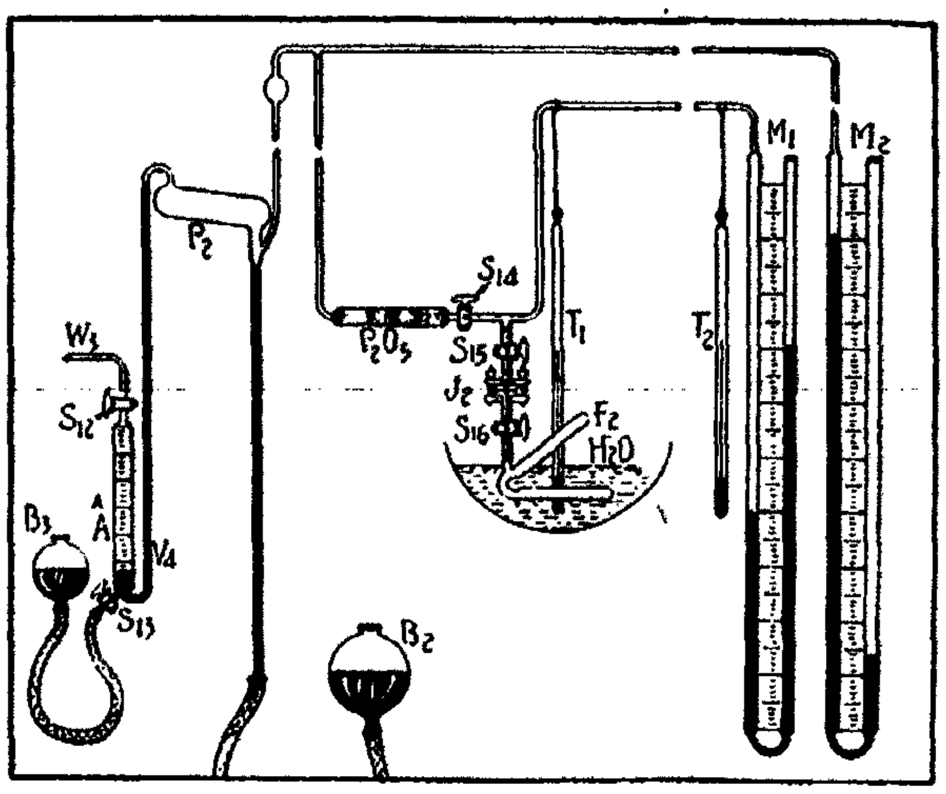

FIG. 1

Samples of the double chloride were prepared in the manner already described (see page 966). Carbon monoxide, which appears to be appreciably soluble in the solution, was completely removed by prolonged boiling of the solution. All phosgene used was carefully purified (see below). Thus prepared, the tube, containing a quantity of the double salt in solution in excess of phosgene, was weighed; it was then clamped in position in the ther-

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[1] A modification of the pump described by Germann and Cardoso; J. chim.phys., 10, 306 (1912).

mostat, and its vapor tension measured; a measured volume of phosgene vapor was then withdrawn, as described, and the vapor tension of the remaining solution measured; and so on to exhaustion of the phosgene; the tube was then weighed again, the loss in weight representing the total weight of phosgene evolved; the tube was finally opened, the dephosgenated salt removed for analysis, and the tube and excess of calcium weighed; thus the weight of dephosgenated salt was arrived at.

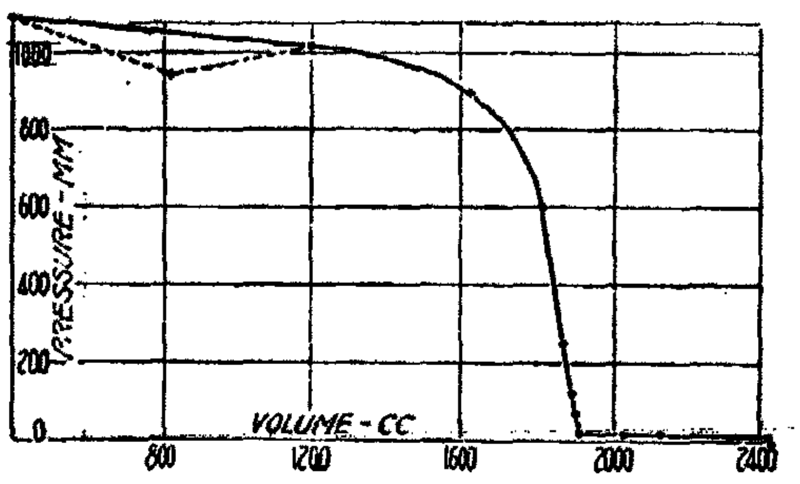

FIG. 2
System: $CaCl_2$, 2 $AlCl_3$—$COCl_2$

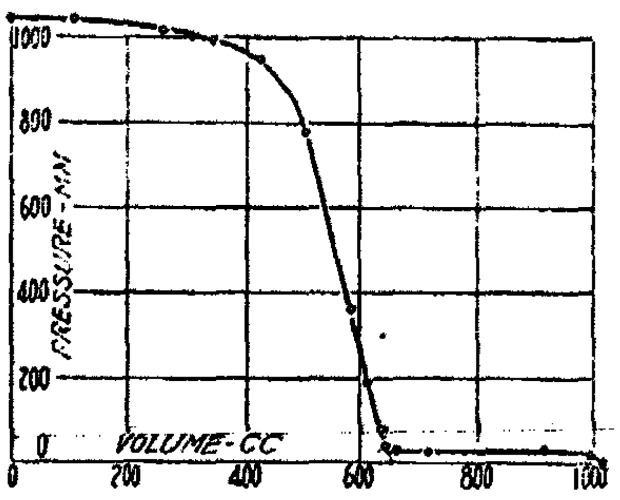

FIG. 3
System: $CaCl_2$, 2 $AlCl_3$—$COCl_2$

The pressure concentration diagrams for samples numbered 17 and 18 are given in Figures 2 and 3. In these curves, the upper, nearly horizontal portion represents the vapor tension of the solution of the double chloride; in the presence of crystals, this should be constant, and hence the curve should be perfectly horizontal; but as already pointed out, (page 967), aluminium chloride is probably present in slight excess, due to incomplete reaction of phosgene with calcium; and hence the vapor tension diminishes as the concentration of this impurity increases. Figure 3 shows one point, at 944.5 mm., considerably below the others on this portion of the curve; when this measurement was made, the solution contained no crystals; but during the subsequent evaporation of nearly 400 cc. of phosgene vapor from the solution, crystals suddenly appeared, and the vapor tension rose to 1013 mm.; the lower point corresponds to a supersaturated solution of the double chloride in phosgene. This is evidence of rather high solubility. However, no solubility determinations have been made.

The second, the descending portion, of the curves, represents the drying of the crystals; in other words, the evolution of adsorbed phosgene from the surface of the crystals; the slope of the curve here probably depends on the size of the crystals, or, what amounts to the same thing, on the surface area per unit of mass.

The final portion of the curves is horizontal, and represents the constant vapor tension during dephosgenation of the crystals; this amounts to about 25 mm. at 19.5°C. The mass of phosgene evolved during this interval was chemically combined with the double chloride as phosgene of crystallization. The calculation follows:—

	Sample No. 17.	*Sample No. 18*
Weight of aluminium chloride,	3.1286 gm.	2.2783 gm.
Weight calcium taken,	0.5463 gm.	0.5378 gm.
Excess of calcium,	0.1159 gm.	0.2125 gm.
Weight calcium reacted,	0.4304 gm.	0.3253 gm.
Weight dephosgenated salt,	4.2790 gm.	3.0282 gm.
Volume of combined phosgene,	521 cc.	375 cc.
Total volume phosgene,	2421 cc.	1021 cc.
Weight of total phosgene,	10.2309 gm.	4.1860 gm.
Moles combined phosgene,	0.02225 mole.	0.01553 mole.
Moles $CaCl_2.2AlCl_3$,	0.01132 mole.	0.008011 mole.
Ratio salt to phosgene,	1:1.965	1:1.939

The ratio of salt to phosgene is thus, in round numbers, 1:2, and the formula of the crystals is therefore

$$CaCl_2.2AlCl_3.2COCl_2.$$

Purification of Phosgene. Figure 4 is a diagrammatic sketch of an all-glass apparatus, as used in this laboratory for the purification of phosgene. The main supply tank (not shown) is a 100 lb. steel container, in which phosgene was supplied by Edgewood Arsenal. The supply valve of this is connected to a 1/4" pipe line, having outlet valves at convenient points in the laboratory; another outlet valve, the exhaust valve, opens from the 1/4" pipe directly into a 3/4" waste pipe, which opens into a 2" standpipe installed as a phosgene waste, extending above the highest part of the laboratory roof. The phosgene pressure in the 1/4" supply pipe, after shutting off the valve at the main supply tank, is released by opening this exhaust valve for a moment.

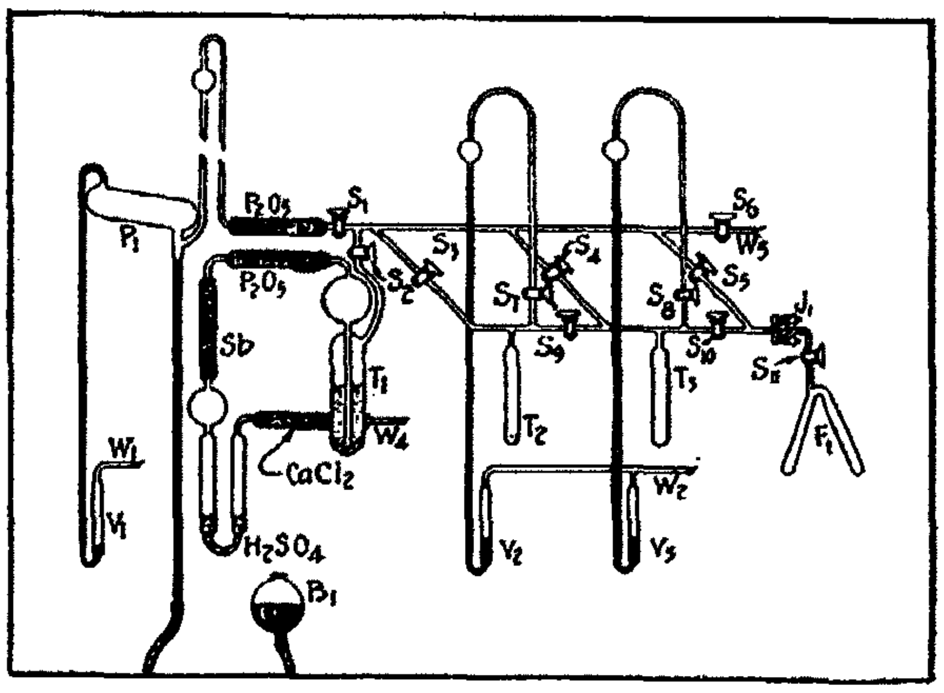

Fig. 4

The glass apparatus is connected to one of the brass supply valves at W_4; De Khotinsky cement is used to make a gas-tight joint with the brass. On being admitted to the apparatus, the gas traverses successively a tube of anhydrous calcium chloride, a sulfuric acid wash bottle, a tube containing antimony powder supported on glass wool, another tube containing alternate layers of phosphorous pentoxide and glass wool, and finally a tube containing a concentrated solution of aluminium chloride in liquid phosgene, T_1; the bulb above this tube must be large enough to prevent the liquid sucking back into the phosphorous pentoxide tube, and is usually made with a capacity of 500 cc., while the total capacity of the tube T_1 is no more than 250 cc.

T_1 is a very useful part of the apparatus, as it provides an auxiliary storage tank for phosgene, and makes the system extremely elastic. The great solubility of aluminium chloride in phosgene and the existence of several phosgenates of this salt combine to yield a solution whose vapor tension is much lower than that of pure phosgene. Baud[1] reports that the pentaphosgenate, $2AlCl_3.5COCl_2$, has a vapor tension of one atmosphere[2] at 30°C., whereas pure phosgene has the same vapor tension at 8°C. Hence under the pressure at which phosgene is supplied from the main supply tank, phosgene readily condenses in T_1, and a bath of ice and water is sufficient to absorb the heat of condensation. Impurities such as HCl, CO, CO_2, for which no chemical absorbent is provided in the gas train, are partially removed here, after closing the supply valve, by boiling off, opening stopcocks S_2, S_3 and S_7 for the purpose. The gases escape by bubbling through the mercury manometer V_2, and are carried off through the tube W_2, which communicates with the exhaust pipe for waste phosgene.

Further purification is carried out in T_2 and T_3; a sample is distilled into T_2 from T_1, using liquid ammonia as refrigerant. The vapor tension at zero at this stage is ordinarily much in excess of 557 mm., the average of the values obtained by Paternò and Mazzucchelli[3], of the somewhat higher values obtained by the Chemical Warfare Service[4], whose value is given by Schaufelberger as 563 mm., and by Atkinson, Heycock and Pope[5] who give the value 568 mm. Volatile gases are pumped off by the action of the water suction pump, which communicates with the apparatus at W_5, through the stopcock S_6; the evolved gases are drawn through bottles containing sodium hydroxide before being discharged by the pump. The vapor tension of pure phosgene at the boiling point of ammonia (−33°) is given by Atkinson, Heycock and Pope as 124 mm.; the loss of phosgene is therefore not great. The vapor tension of the residual phosgene is measured from time to time, by surrounding the liquid with an ice bath, and making an approximate reading on the manometer, V_2. When the vapor tension has been reduced to a value approximating 560 mm., three or four fractional distillations are carried out between T_2 and T_3, both the first and last fractions being discarded. The liquid phosgene may be kept for some days in T_2 or T_3, by closing S_7 or S_8, and providing each of the stop cocks guarding the storage tube with clamps.

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[1] Compt. rend. **140**, 1688 (1905).

[2] We have made an initial study of the pressure-concentration diagram of this system, but as the results are not in entire agreement with those obtained by Baud, the problem is being subjected to closer scrutiny.

[3] Gazz. chim. ital., **50** I, 30 (1920).

[4] Schaufelberger: Thesis, Stanford University, (1920); based on Edgewood Arsenal Chemical Laboratory Report No. 223.

[5] J. Chem. Soc., **117**, 1410 (1920).

The Faraday tube or other trial tube F_1 may be attached to the apparatus at J_1, by means of the universal flat joint and clamp. Any part of the apparatus may be evacuated with the water suction pump, by operating stopcock S_8, or with the mercury pump by operating stopcock S_1. Phosgene discarded through the mercury pump is discharged through W_1 into the exhaust pipe for phosgene.

Ordinary rubber grease is very soluble in phosgene; this fact is unimportant when pressures are low; but whenever the pressure within the apparatus approaches or exceeds one atmosphere, the grease is more or less rapidly dissolved away. Stopcocks lubricated by dusting with phosphorous pentoxide, and exposing to the atmosphere until moist, work very well; they last much longer when access of air is prevented by a ring of rubber grease at the top and bottom[1].

Conclusion. In the presence of aluminium chloride, phosgene reacts with a number of metals, forming double chlorides. Magnesium and calcium especially react readily, the first yielding a two liquid layer system when cooled, the second a crystallizable product that is very soluble. The crystals were found to have the formula $CaCl_2.2AlCl_3.2COCl_2$. The pressure concentration diagram was determined for this system, and the decomposition pressure of the phosgenate at this temperature found to be 25 mm. approximately. A method of purifying technical phosgene has been described.

Acknowledgement. We wish to take this opportunity of expressing our appreciation to the Chemical Warfare Service for the generous supply of phosgene contributed for this research.

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California.

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[1] Guye and Drouginine: J. chim. phys., 8, 503 (1910).

CATALYTIC ACTION OF NITROUS ACID

BY WILDER D. BANCROFT

In 1842 Millon[1] showed that copper reacts with ten percent nitric acid at 20° only when nitrous acid is present in the solution. The reaction is prevented by the presence of some substance, such as ferrous sulphate, which removes the nitrous acid as fast as it is formed. When the nitric acid is free from nitrous acid, the reaction with the copper can be produced either by passing in a few bubbles of nitric oxide gas or by adding a few drops of a solution of a metallic nitrite. Millon considers that "copper, mercury, and silver react with nitrous acid, forming nitrites which are decomposed by the nitric acid forming nitric oxide which then reacts with the nitric acid to form nitrous acid, after which the cycle repeats."

Russell[2] says that "it has long been believed that the great activity of nitric acid towards many metals was owing rather to its containing a small amount of nitrous acid than to the affinities of the acid itself; and, with regard to silver, this undoubtedly is the case, and the following experiments show that it holds good even with very dilute solutions of nitric acid. Two similar pieces of silver foil, both weighing 0.3 gram, were placed in similar tubes, each with 5 cc. of dilute nitric acid containing only 1.6 per cent of HNO_3. Through one of these solutions only two small bubbles of nitrous acid were passed; both liquids were then corked up, and left to stand for forty-six hours, and the amount of silver dissolved was estimated: in the solution through which the nitrous acid had passed, 0.0262 gram was found; in the other one 0.0093. If stronger acid solutions be used, this action of the nitrous acid is still more marked. Two similar pieces of silver foil, weighing about two grams each, were put, as in the above experiment, into dilute nitric acid, but containing 17.5 percent of HNO_3 in place of 1.6 percent. Two or three bubbles of nitrous acid were passed through one liquid only; immediately the silver in this liquid became covered with minute bubbles, and after twenty minutes the whole of the silver was dissolved, whereas the other piece of foil, after exactly the same length of time, was hardly attacked at all, for the liquid, on treating it with a chloride, gave only a slight cloud of silver chloride. Nitric oxide passed into the solution gives, of course, similar results. There is another curious reaction with regard to the dissolving up of the silver in nitric acid. Two similar pieces of silver were placed in diluted nitric acid, but still so strong as to dissolve silver, that containing 17.5 percent of HNO_3, for instance, and hydrogen was made to bubble through one of the tubes with silver solution, while through the other the hydrogen streamed without bubbling through the liquid. In one experiment it was found that after an hour the silver in the tube through which the hydrogen did not bubble was entirely

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[1] Compt. rend. 14, 904 (1842).

[2] J. Chem. Soc. 24, 8 (1874).

dissolved, and in the other one the metal was not attacked to an appreciable extent by the acid, for the liquid gave only a faint cloud on adding a chloride, the bubbling of the hydrogen through the liquid having therefore protected the silver. This protective action is, however, in no way peculiar to hydrogen; air will act in the same manner. The gas sweeps away any nitric oxide and keeps the nitric acid pure.

"The dissolving up of the silver after it has been precipitated by the hydrogen from silver nitrate may then be satisfactorily explained, if there be any reason for the formation of only a trace of nitrous acid. A trace of this oxide of nitrogen is sufficient to start the action of the acid on the silver, and, once started, the action increases very rapidly in intensity. The reaction which takes place is probably something of this kind. The nitrous acid attacks the silver, forming silver nitrite, nitric oxide, and water, the nitric oxide thus formed reducing hydric nitrate and forming more nitrous acid. Thus the action gets quicker and quicker, and may be started by the addition of a lower oxide of nitrogen. The point still remaining to be explained is, then, how the first trace of nitrous acid is formed. Assume that to be formed, and with this cumulative action the rest is easy of explanation; and certainly if, as appears to be the case, pure hydric nitrate has little or no action on silver, at all events when dilute, it is not obvious why it should be formed."

Veley[1] sums up his own results by saying that "the metals, copper mercury and bismuth do not dissolve in nitric acid of about thirty percent concentration, and heated to a temperature of about 30°C, provided that nitrous acid is neither present initially nor formed subsequently. To prevent these contingencies it is necessary to add a small quantity of some oxidizing substance such as hydrogen peroxide or potassium chlorate, or as less efficacious, potassium permanganate, or to pass a current of air, or lastly such a substance as urea, which destroys the nitrous acid by its interaction.

"If the conditions are such that these metals dissolve, then the amount of metal dissolved and the amount of nitrous acid present are concomitant variables, provided that the nitric acid is in considerable excess. Change of conditions, such as concentration of acid and variation of temperature, which increase the former increase also the latter. Again, if the oxides of nitrogen and nitrous acid formed are kept within the liquid by enclosing it within a sealed tube, then the amount of metal dissolved in unit time is also increased."

Veley interprets his results on the assumption that nitrous acid is reduced readily to nitric oxide. "The experiments detailed above for the metals, copper, mercury, and bismuth, to which, according to Russell's experiments, silver must also be added, have established the following facts:—(1) the primary change is that between the metals and nitrous acid; (2) no gas is evolved at first from the surface of the metal; (3) the amount of nitrous acid increases up to a constant and maximum proportion; and (4) those conditions which increase the amount of metal dissolved per unit time, are equally those conditions which increase this constant proportion of nitrous acid. If then a trace of nitrous acid becomes once formed, and if, also, the quantity of nitric acid

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[1] Phil. Trans. 182 A, 279 (1891).

is present in very considerable excess, it would appear that these results may be explained as follows:—(1) the metal dissolves in nitrous acid to form the metallic nitrite and nitric oxide; (2) the nitrite formed is decomposed by the excess of nitric acid to reproduce the nitrous acid; and (3) the nitric oxide formed in (1) is not evolved as such, but reduces the nitric acid or the nitrate to produce a further quantity of nitrous acid. These changes may be represented thus, taking copper for example:

(1) $Cu+4\ HNO_2=Cu(NO_2)_2+2\ H_2O+2\ NO$
(2) $Cu\ (NO_2)_2+2\ HNO_3=Cu(NO_3)_2+2\ HNO_2$
(3) $2NO+HNO_3+H_2O=3\ HNO_2$.

"The same equations apply to the other metals, *mutatis mutandis.* The condition of the increase in amount of the nitrous acid is satisfied, for at the start four molecular proportions take part, while five are ultimately produced; the non-evolution of nitric oxide in the earlier stage of the change is also accounted for. But when the amount of nitrous acid has reached a certain point, the reverse of equation (3) takes place, and the nitric oxide is evolved from the liquid.

(4) $3\ HNO_2=HNO_3+2\ NO+H_2O$.

"At this point the nitrous acid is decomposed as fast as it is formed, the amounts of the reactions (3) and (4) per unit time being doubtless dependent as in other similar cases, upon the relative masses of the nitrous and nitric acids, upon the temperature and other conditions of the experiment.

"This explanation is, however, only valid provided that the mass of nitric acid be in very large excess over that of the nitrous acid, for it is evident from the experiments described above, that, if there is no very great difference between the masses of the two acids, the nitric acid serves to impede rather than to promote the chemical change, a result which is probably due to the greater stability of nitrous acid in the presence of a small quantity of nitric acid.

"There yet remains one further point; if these metals by themselves do not dissolve in dilute nitric acid by itself, by what manner of means is the necessary nitrous acid formed initially? It is, of course, possible that the metal will enter into chemical change with an amount of nitrous acid less than that detected by the meta-phenylene diamine; it is also possible that some metallic impurity forms with the metal a couple which electrolyzes the nitric acid, thereby producing nitrous acid. As regards this latter point, it is worthy of remark that, of the metals experimented with, mercury was less susceptible of chemical change than copper, and copper in its turn than bismuth. This order is equal to that of their probable degree of purity.

"A few experiments were accordingly made to determine the amount of a foreign metal which could be added to pure mercury without promoting its reaction with nitric acid. These showed that one part in a thousand of pure copper and one part in eight hundred of pure silver added to mercury did not render the latter susceptible of chemical change, even with nitric acid of 30.5 percent concentration, and heated to 28.5°, provided that both metal and acid were stirred continually. If both were at rest, then, as in the previous experiments, the change commenced immediately."

It is to be noted that Veley gives no proof for this explanation. It is merely an attempt to account for the facts, and the explanation was apparently the only one that occurred to him. As a matter of fact, there is nothing in his experiments or in those of Russell which proves his first contention that "the primary change is that between the metals and nitrous acid." What the experiments prove is that no appreciable action takes place when no nitrous acid is present and that the rate of reaction is a function of the concentration of the nitrous acid. It is not unreasonable to make the hypothesis that the reaction is between the metal and the nitrous acid; but that is quite a different matter from proving it. The reaction between methyl alcohol and acetic acid takes place very slowly at low temperatures. The rate of reaction is a function of the hydrochloric acid added and consequently Petersen[1] concluded that there was a reaction between methyl alcohol and hydrochloric acid to form methyl chloride. As Tafel[2] showed, it was merely a case of the catalytic action of hydrochloric acid. It will be shown from Ihle's work that nitrous acid is a catalytic agent and does not react directly with the metals.

Veley's second equation is quite superfluous because cupric nitrite would not be formed in the first place. Veley's real assumption is not that copper reacts with nitrous acid to form copper nitrate; but that nitrous acid is the hydrogen depolarizer. If Veley had worded his assumption properly, he would have seen that the intermediate formation of copper nitrite was an absolutely superfluous postulate.

One cannot blame Veley for assuming that nitric oxide is a reduction product of nitrous acid. Too many other people have thought the same thing. Since we now know,[3] as was shown by Armstrong[4] nearly fifty years ago, that nitric oxide is not one of the direct reduction products of nitrous acid, Veley's assumption becomes hopelessly improbable.

While it is perhaps not fair to criticize Veley severely for having failed to appreciate Armstrong's work, he should have known that nitric oxide would have escaped to a greater or lesser extent in an open vessel. He should also have noticed that his own reasoning brought nitrous acid out as chiefly a catalytic agent. If we combine Veley's three equations, we get

$$Cu+4\ HNO_2+3\ HNO_3=Cu\ (NO_3)_2+5\ HNO_2+H_2O.$$

If we cancel the four molecules of nitrous acid, we have

$$Cu+3\ HNO_3=Cu\ (NO_3)_2+HNO_2+H_2O.$$

This does not preclude the possibility of nitrous acid forming some intermediate compound in the course of its catalytic action; but it does make it incumbent on somebody to prove that the intermediate reaction does take place.

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[1] Z. physik. Chem. 16, 385 (1895); 20, 33 (1896).

[2] Z. physik. Chem. 19, 592 (1896).

[3] Bancroft: J. Phys. Chem. 28, 481 (1924).

[4] J. Chem. Soc. 32, 56 (1877).

In a later paper Burch and Veley[1] attempt to show that nitrous acid is a stronger oxidizing agent than nitric acid and would therefore be reduced first, though this is not compatible with a marked building-up of the concentration of nitrous acid.

Their general conclusions are as follows:—

"1. The experiments detailed above show that when the metals, copper, silver, bismuth, and mercury are introduced into purified nitric acid of varying degrees of concentration, and a couple made with platinum, the electromotive force of such a cell increases considerably until it reaches a constant and (in most cases) a maximum value. This rise of electromotive force is attributed to the production of nitrous acid by the decomposition of the nitric acid, and the final value is considered to be due to the former acid only, while the initial value is due for the most part to the latter acid, though it is affected to a remarkable degree by the amount of impurity of nitrous acid either initially present or produced by minute and unavoidable uncleanliness of the metallic strips and the containing vessel.

"2. If nitrous acid has been previously added to the nitric acid, then the maximum electromotive force is reached at once.

"3. If the conditions, namely, increase of temperature, of impurity, and of concentration of acid, are such as could favour a more rapid production of nitrous acid, then the rise of electromotive force is concomitantly more rapid.

"4. Conversely, if the conditions are unfavourable to the production of nitrous acid, the rise of electromotive force is less rapid.

"5. If any substance, such as urea, be added, which would tend to destroy the nitrous acid as fast as it may be formed, then the rise of electromotive force is extremely slow, being dependent upon the number of molecular impacts of nitrous acid upon the surface of the metal. Thus the results obtained by the electrometer and of the chemical balance are in every way confirmatory, the one of the other. These results open out the further question as to whether the electromotive force of batteries, in which concentrated nitric acid forms an ingredient, is dependent not upon the nitric acid *per se*, as hitherto supposed, but upon the nitrous acid present in the fuming nitric acid, and formed also by the reduction of the acid by the hydrogen, which would otherwise be given off from the zinc and sulphuric acid."

These results would be very convincing if they were right; but this seems not to be the case. Ihle[2] found that a nitric acid solution containing nitrous acid is a less strongly oxidizing solution, than one containing no nitrous acid, though the rate of oxidation is increased by the addition of nitrous acid. "The two English investigators [Burch and Veley] always observed a rise of the electromotive force to a constant (maximum) value and also found that the time of this increase depended exclusively on the presence or absence of nitrous acid, addition of this acid causing a very considerable shortening of the time necessary to reach the maximum value. Conditions such as higher

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[1] Phil. Trans. **182** A, 319 (1891).
[2] Z. physik. Chem. **19**, 577 (1896).

temperature increased concentration of the nitric acid, etc., which favor the formation of nitrous acid, accelerate the increase of the electromotive force, while substances, such as urea, which decompose the existing or nascent nitrous acid, retard the increase of the electromotive force. They account for these phenomena by the assumption that the lower initial value of the electromotive force is a measure of the potential of the nitric acid, while the higher final value measures the potential of the nitrous acid. The rate of increase of the electromotive force depends solely on the number of nitrous acid molecules which are formed from the nitric acid. According to this point of view, the finally reached maximum of the electromotive force should be higher, the more nitrous acid there is in the nitric acid. Exactly, the opposite is true, as was observed by Burch and Veley; and I have myself confirmed this result. In order to clear up this contradiction Burch and Veley[1] assumed that nitrous acid ready formed is not so active a material as nitrous acid in the alternative process of formation and decomposition. The inadequacy of this hypothesis here is evident."

Ihle found that "nitrous acid lowers the potential of nitric acid, the lowering being greater the more nitrous acid is added. On the other hand the addition of nitrous acid increases the rate of oxidation of the nitric acid and therefore decreases very markedly the time necessary for a dilute nitric acid solution to give the maximum value. If one adds nitrous acid to a very dilute nitric acid before this solution gives its maximum value, the addition apparently causes a rise of potential. The resulting value is lower, however, than that which would have been reached in time by the nitric acid solution alone.

"The addition of urea causes the destruction of nitrous acid and raises the potential of the nitric acid. Addition of urea to solutions containing less than 35-40% nitric acid causes an apparent lowering of the potential, because at these concentrations the rate of change of the nitric acid decreases very much, the Grove cell changing to the Smee cell at about this concentration. Since the measurement of electromotive force involves some flow of current because the capacity of the capillary electrometer is fairly large, every observation is accompanied by some transfer of electricity, even though a very small one, and consequently by some chemical change. If the chemical changes take place very slowly, the measurements of electromotive force may be affected seriously thereby."

On the assumption that the potential of the normal calomel electrode is −0.560 volt, Ihle makes the value for platinum in 95% nitric acid −1.52 volt, in 6% nitric acid −1.23 volt, and in nitrous acid of unspecified concentration −0.95 volt. Nowadays the signs would be positive and not negative.

We can see in another way that there is nothing to Veley's assumption that the metal dissolves to nitrite. If we add nitrous acid to the Grove cell or to the Smee cell, we increase the depolarizing action of the nitric acid; but no metal dissolves in the nitric acid solution and consequently there is no formation of nitrite. The behavior of these two cells was discussed by Ihle[2]

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[1] Phil. Trans. **182** A, 330 (1891).

[2] Z. Elektrochem. **1**, 174 (1895).

in an earlier paper. "If one dilutes the concentrated nitric acid in the Grove cell gradually and measures the electromotive force (of the cell at the same time, one finds that the electromotive force) remains nearly constant until the concentration of the nitric acid drops to about 38%. At slightly lower concentrations the cell shows, though at first only for a very short time, a changed and much smaller electromotive force than the 1.8 volt characteristic of the Grove cell; it corresponds rather to the 0.7 volt of the Smee cell. If one dilutes the nitric acid more and more, the time during which the cell stays at the lower potential increases until at a nitric acid content of 27-28% the element keeps the low electromotive force of the Smee cell permanently.

"To carry out this experiment, one pours dilute nitric acid into an ordinary battery jar and puts into this two small, porous cups. In one of the cells is placed an amalgamated zinc rod and a zinc sulphate solution while a platinum electrode and the nitric acid to be tested are placed in the other porous cup. The two poles of the cell are connected through a galvanometer. Since the resistance remains the same in all the experiments, changes in the electromotive force of the cell will show as changes in the deflection of the galvanometer.

"It seemed probable that the peculiar relation between the concentration of the nitric acid and the electromotive force of the cell was due to nitrous acid present in the nitric acid solution or formed in it while the circuit is closed. This guess has been confirmed. If one adds a small amount of potassium nitrite to a cell containing less than 28% nitric acid and therefore giving permanently the potential of the Smee cell, the galvanometer needle swings at once to the deflection corresponding to the electromotive force of the Grove cell. If one removes the nitrous acid again by adding potassium permanganate,[1] hydrogen peroxide, or urea, the galvanometer needle goes back at once to the original value which corresponded to the Smee cell.

"Just as one can make dilute nitric acid active as a depolarizer by means of nitrous acid, so one can also remove the depolarizing power of concentrated nitric acid containing more than 38% HNO_3, by removing continuously the small amounts of nitrous acid which are always present in so strong nitric acid by means of urea or potassium permanganate and can thereby convert a Grove cell into a Smee cell. With very concentrated acid containing 50-60% HNO_3, the conversion is only temporary because more nitrous acid forms soon. From this it follows that nitrous acid is the real depolarizer in the Grove cell and not nitric acid as is usually assumed, or at any rate, that it is only in presence of nitrous acid that the oxygen of the nitric acid reacts with hydrogen set free electrolytically at the platinum.

"The question arises as to how this action takes place and it seems probable that we are dealing with a case of catalysis. Nitrous acid plays the part of a catalyzer here just as it does in other cases, such as the action of nitric acid on metals studied by V. H. Veley."

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[1] On adding potassium permanganate there is at first an increase in electromotive force corresponding to the high potential of permanganic acid; but the galvanometer needle goes back to the value corresponding to the electromotive force of the Smee cell as soon as the permanganic acid in immediate contact with the platinum electrode is used up.

I think that this critical study of the literature shows that nitrous acid is not the actual depolarizer but that it acts as a catalytic agent making the nitric acid active. The next question is as to the way in which nitrous acid acts and I think that the answer to this question is suggested by the previously quoted statement by Burch and Veley[1] that "nitrous acid ready-formed is not so active a material as nitrous acid in the alternative process of formation and decomposition." If one substitutes nitric acid for nitrous acid in this statement, we have made a real step forward. I have pointed out in another paper[2] that any reaction between so-called saturated compounds involves either a preliminary dissociation which means the breaking of a regular bond, or a preliminary association which means the opening of a contravalence or residual valence. In the case of a solid catalytic agent the thing of real importance is not the formation of a definite intermediate compound or the formation of an adsorption complex; but is the formation of the free radical, taking the term in its broadest sense—which is the real reacting substance. In so far as we can duplicate photochemically the action of a contact catalyst this must be so, because light can activate a substance only by opening a normal valence or a contravalence. We can word this in a different way, if it will make it clearer to anybody, by saying with Baly[3] that activation means opening up fields of force, because "it is a necessary deduction that the condensing together of the lines of force must result in a decrease of chemical activity, and, indeed, it would seem to follow that the true chemical affinity of any molecule cannot be exhibited until the condensed systems of force lines within each molecule have been unlocked or opened by some means."

"It is evident that the condensing together of the lines due to the force fields round the component atoms of a molecule must result in an enormous decrease in the reactivity of the molecule, and, in fact, it may be said that such a condensed system cannot react unless it previously be opened or unlocked by some means. For example, the well-known cases described by Baker, when pure, dry substances, such as ammonia and hydrogen chloride, lime and carbon dioxide, do not react together are doubtless due to the fact that the force fields of the molecules are so condensed together that no reaction takes place when they are brought together. The presence of water is required in order to open these systems sufficiently for the reaction to proceed, the merest trace of water being enough to catalyze the whole reaction. Again, the converse cases of the vapors of ammonium chloride and mercurous chloride may be explained in the same way, for these molecules evidently possess their force fields so condensed that increase of temperature alone is not sufficient to open them, and the vapor densities correspond with those of the undissociated molecules. The presence of water, however, opens the condensed fields sufficiently for the molecules to dissociate under the influence of higher temperatures.

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[1] Phil. Trans. **182** A, 330 (1891).

[2] Bancroft: Ind. Eng. Chem. **16**, 270 (1924).

[3] J. Chem. Soc. **101**, 1469, 1475 (1912).

"The general phenomenon of catalysis is capable of explanation on these lines, for a catalytic agent may be defined as one which opens the condensed system of the reacting substance or substances so that their chemical reactivity is enhanced. Negative catalysis is equally capable of explanation, for a negative catalyst is simply a type of substance which tends to close up the condensed systems, and thus counteract the action of the solvent. Specific evidence of such closing of the molecular systems have been observed from absorption spectra, as will again be mentioned.

"It follows from the above that any chemical reaction must take place in at least two stages. First, the reacting substances must have their condensed systems opened up, and, secondly, these opened systems will react together to give the expected compound. It is clear that these stages should be possible of observation, and that, in the event of their taking place, they should evidence themselves in some way. There is no doubt that the explanation of the color changes of the aromatic aminoaldehydes and ketones when treated with alcoholic hydrogen chloride are due to these stages in the reaction. When, for example, o-aminoben-zaldehyde is dissolved in alcohol, the condensed system is partly opened, owing to its penetration by the force lines due to residual affinity of the alcohol. On the addition of hydrogen chloride, the final product is, of course, the hydrochloride; but the base in the form in which it exists in alcoholic solution does not itself react with the acid to give the salt. It passes through an intermediate phase when it is opened up to a more complete stage, and it is this intermediate phase that reacts with more acid to form the salt. The intermediate phase has a yellow or red color with a characteristic absorption band[1] as has already been described."

If we apply this point of view to the case that interests us at the moment, we see that a dynamic equilibrium must represent a more active state than a static one. In the case of the reversible reaction

$$HNO_3 + HNO_2 \rightleftarrows 2\ NO_2\ (\text{or}\ N_2O_4) + H_2O,$$

the nitric acid is continually going over to nitrogen peroxide and being formed from the latter. During the moments of change the nitric acid, the nitrogen atom, or some radical containing nitrogen and oxygen must be in a different state from what it would be if no nitrous acid were present and if this reaction were not taking place. If the particular intermediate stage involved in this reaction is one which permits more rapid reaction with nascent hydrogen, our problem is solved. Actually, we have merely formulated our old problem in a new way.

If this point of view is correct, we are dealing with a general problem and all cases of dynamic equilibrium should be more reactive along certain lines than if no dynamic equilibrium were involved. This generalization is very important if true and I am putting it forward in this half-baked form in the hope of getting information as to previous formulations of the same idea which I am quite certain have been made, and of getting information as to innumerable cases where this generalization will prove helpful.

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[1] Baly and Marsden: J. Chem. Soc. 93, 108 (1908).

Electrolytic dissociation is a special case under this general head. The dynamic equilibrium represented by the equation

$$RX \rightleftarrows R^{\cdot} + X'$$

gives us forms which are much more reactive along certain lines than in the case of a non-ionizing solvent where this special equilibrium occurs at most to a negligible extent.

In a recent paper Norris[1] says that one of the major problems being studied at the Massachusetts Institute of Technology is "the change in reactivity of atoms and groups in organic compounds as affected by changes within the molecule and in its environment. Relative reactivities are measured by comparing the rates at which the several members of a series of compounds of the same type react with a second compound which is the same in all cases. In this way the effect of changes within the molecule can be measured. The influence of the presence of substances outside the molecule, such as solvents or catalytic agents can be measured in the same way. The solvent or catalytic agent affects the bonds in the activated compounds in the same way that changes within the molecule bring about this effect. In many cases compounds made up of the catalyst and the activated molecule have been isolated. It is highly probable that in cases where such addition compounds are not formed, a molecular attraction exists, which results from residual affinities. Two molecules, when brought together, must exert an influence, one on the other, and this must result in a change in the attractions between the atoms within each molecule. Solvents have a marked effect on the rate at which a given reaction proceeds. From the foregoing point of view, they act as true catalysts by altering the strength of the affinities between the atoms in the dissolved molecule. When the changes set up in the affinities lead to increased reactivity, the added substance is a positive catalyst. If, on the other hand, the reactivity is reduced, the substance functions as a negative catalyst. The normal rate of reaction between two molecules occurs when these two kinds alone are present."

Norris belongs rather to the Michael school than to the Nef school of organic chemists and he prefers to think in terms of association rather than of dissociation. The important thing to note, however, is that there is no evidence that the addition compound is the reacting substance. All the phenomena can be explained equally well, so far as we now know, on the assumption that the radicals, produced as the addition compound is formed or decomposed, are the reacting masses. This would mean that it is the reaction which causes the activation and that the reaction product is important only in so far as it makes the reaction possible. We have seen that nitrous acid is not the depolarizer under ordinary conditions when metals are attacked by nitric acid solutions. Consequently we are forced, at any rate for the present, to postulate that the activation is due to the reaction. Of course, one must not claim that nitrous acid never acts as a depolarizer because that would make impossible the reduction of nitrous acid to hyponitrous acid, hydroxyl-

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[1] Ind. Eng. Chem. 16, 184 (1924).

amine, and ammonia. All that Ihle has shown and all that I am claiming is that we can ignore the possible reduction of nitrous acid under the conditions prevailing in Veley's experiments.

The general results of this paper are:—

1. Under the conditions prevailing in Veley's experiments, nitrous acid is not as strong an oxidizing agent as nitric acid and does not act as the depolarizer.

2. Nitrous acid acts catalytically in activating nitric acid.

3. It seems probable that the activation of nitric acid depends on the dynamic equilibrium represented by the equation

$$HNO_3 + HNO_2 \rightleftarrows 2\ NO_2 + H_2O.$$

4. This interpretation brings the action of nitrous acid in line with the action of light and in line with the action of solid catalytic agents.

5. If a state of dynamic equilibrium involves activation in certain directions, this must be a general phenomenon and must be shown to occur in all such cases.

Cornell University.

THE DECOMPOSITION OF HYDROGEN IODIDE[1]

BY H. AUSTIN TAYLOR

The general problem of chemical reaction and reactivity has received considerable attention during the past decade, and numerous theories[2] have been advanced which have attempted with varying success, to account for the many facts already observed. The treatment of reactivity from the point of view of chemical kinetics has met with apparent success in numerous cases but the time is rapidly approaching when it will be essential to verify practically all the data accumulated in the light of more recent advances before they can be used to confirm a theory. The writer has recently[3] called attention to the necessity of a modification of the earlier ideas of the general stability of molecules in view of the great influence of polar substances on various reactions, and on this account considerable doubt must be held regarding data with respect to supposedly homogeneous reactions.

The recent attempts to obtain a solution of the problem of unimolecular reaction velocities remain open owing to the lack of data wherewith to confirm them. All the reactions which were supposed until recently to be unimolecular have now been shown to be at least bimolecular and except for examples of radioactive change (for an explanation of which the aid of such theories is unnecessary and inapplicable) not one example of unimolecular decomposition can be cited. Resulting from this and from the extremely general influence of catalysts, recent work by Rideal, Norrish and others[4] has led to the conclusion that most chemical reactions are catalytic in nature, and that the number of bimolecular reactions which are known to occur in the gaseous state without a catalyst is rapidly decreasing. Attempts at a theoretical evaluation of bimolecular reaction velocities have made use in many cases[5] of data of reactions which were assumed to be homogeneous gas reactions but which are now being shown not so.

In the attempt by Lewis to calculate the velocity constant of the bimolecular decomposition of hydrogen iodide, although, as Dushman has pointed out, the success of the result in no wise confirms the radiation hypothesis, the agreement between calculated and observed velocity constants is taken as satisfactory. An empirical factor for the distance within which two molecules approach during collision is employed in the deduction, a very slight change in which would cause complete non-agreement between the calculated and observed reaction velocities. In the calculations of Dushman, the heats of acti-

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[1] Contribution from the Laboratory of Physical Chemistry. Princeton University.

[2] Trautz: Z. anorg. Chem., **106**, 81 (1909); Lewis: J. Chem. Soc., **105**, 2330 (1914)' Perrin: Ann. Phys. **11**, 5 (1919); Dushman: J. Am. Chem. Soc., **43**, 397 (1921).

[3] J. Phys. Chem., **28**, 510 (1924).

[4] J. Chem. Soc., **123**, 697, 3006 (1923).

[5] Lewis: J. Chem. Soc., **113**, 471 (1918); Dushman: loc. cit.

vation at various temperatures are obtained which show no falling trend as would be expected from the definition of heat of activation, the mean value being compared with that obtained from the average temperature coefficient of the observed velocity constants. The data employed in both cases are those due to Bodenstein[1], on the assumption that the velocity constants therein obtained pertain only to the purely gaseous decomposition of hydrogen iodide. One of the main results of this investigation is that in glass vessels this decomposition is not a purely gaseous reaction but is influenced effectively by the surface in contact with the gas phase. Consequently it would seem that the data are inadequate for the purpose required and the agreement obtained between observed and calculated results fortuitous. Nor is it possible at the present time to make use of any data whereby such calculations may be unequivocally tested. In a forthcoming textbook[2] Edgar has considered the mass action equilibria in the following gaseous systems, complete references of which are also given:

(1) $H_2+CO_2 \longrightarrow CO+H_2O$
(2) $N_2+O_2 \longrightarrow 2NO$
(3) $CO+1/2O_2 \longrightarrow CO_2$
(4) $H_2+1/2O_2 \longrightarrow H_2O$
(5) $N_2O_4 \longrightarrow 2NO_2$
(6) $NO_2 \longrightarrow NO+1/2O_2$
(7) $I_2 \longrightarrow 2I$
(8) $(CH_3COOH)_2 \longrightarrow 2\,CH_3COOH$
(9) $1/2N_2+\frac{3}{2}H_2 \longrightarrow NH_3$
(10) $SO_2+1/2O_2 \longrightarrow SO_3$
(11) $HCl+1/4O_2 \longrightarrow 1/2Cl_2+1/2H_2O$

In the majority of these reactions no data are available of actual reaction rates wherewith a direct test of the mass action expression may be obtained. In those cases where data are available it has been shown recently that such are not reliable if interpreted as purely gaseous reactions, for example in the case of the oxidation of hydrogen to steam and of carbon monoxide to carbon dioxide the influence of water vapour has been indicated previously and no reaction velocity measurements are available in absence of water vapour. Similarly in the synthesis of ammonia, all available velocity data have been obtained in presence of various catalysts. With reference to the more recent reactions studied, Rideal[3] has shown that the formation of hydrogen sulphide is influenced by the surface of the sulphur undergoing reaction, whilst Daniels[4] points out that the decomposition of nitrogen pentoxide is autocatalysed by nitrogen dioxide.

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[1] Z. physik Chem., **29**, 295 (1899).

[2] "Treatise on Physical Chemistry." Vol. I Chapter VIII. (1924).

[3] J. Chem. Soc., **123**, 704 (1923).

[4] J. Am. Chem. Soc., **42**, 1131 (1920); **43**, 53 (1921); **44**, 757 (1922).

The conclusion is to be drawn therefore, that for the aforementioned theories of bimolecular gaseous reactions, as also for the law of mass action as applied to such reactions, no evidence is available whereby a direct test of the deductions may be made.

Experimental

The general method adopted to study the decomposition of hydrogen iodide was a dynamic one, pure hydrogen iodide flowing at a constant rate through a tube kept at constant temperature, the effluent gases passing into an aqueous solution of potassium iodide, the resulting iodine and hydriodic acid being titrated with standard sodium thiosulphate and potassium hydroxide respectively. From these data the total amount of hydrogen iodide passing in a given period of time (twenty minutes was found to be a convenient time and was employed throughout) and the percentage decomposition could be calculated, as also could the reaction velocity knowing the volume of the tube in the furnace.

Pure hydrogen iodide was prepared by treating red phosphorus and iodine with water in the usual manner, purified by passing through moist red phosphorous and through a U-tube kept in an ice bath to remove further condensible products, and finally dried over phosphorus pentoxide. The gas was then collected in the holder by immersing this in a bath of solid carbon dioxide and ether. When sufficient solid hydrogen iodide had been collected the holder was sealed and kept in the carbon dioxide bath.

In making an experiment the holder was allowed to warm up to 0°C and maintained thereat by immersing in an ether bath in melting ice. This developed a pressure in the holder amounting to approximately four atmospheres and by allowing the gas to flow slowly through a side tube having a fine capillary which allowed about twenty cubic centimetres to pass per minute, a constant flow of gas could be maintained as long as any liquid hydrogen iodide remained in the holder. This side tube was connected to the reaction tube inlet by a short piece of rubber tubing. The reaction tube was fixed in the centre of an electric furnace which could be maintained at constant temperature to within ±1°C. The outlet of this tube had a ground-glass joint to which could be attached the potassium iodide absorber.

Preliminary experiments having shown conclusively that slight traces of oxygen in the reaction tube caused considerable deviations in the constancy of the results, the hydrogen iodide gas was allowed to pass through the tube for about half an hour before any run was commenced, traces of oxygen, both in the reaction tube and the holder being thereby removed by reaction with the gas, the resulting iodine and hydriodic acid being absorbed in aqueous potassium iodide. After such a period, when equilibrium had been obtained in the normal decomposition of the gas, the potassium iodide absorber was rapidly changed and the hydrogen iodide allowed to flow for twenty minutes, the resulting solution being then titrated as stated. The entire glass apparatus used throughout the work was made of pyrex, the glass powder being made by grinding pyrex tubing.

Results and Discussion

The first experiments made were at temperatures of 480 and 500°C, using a reaction tube of 122 cubic centimetres volume having an inside area of approximately 600 square centimetres. The results obtained were:

TABLE I

Temp. in °C	Total HI in g.	HI decomposed in g.	Percent decomp.	Mean.
480	2.5767	0.0332	1.29	
480	2.4967	0.0327	1.31	
480	2.5438	0.0308	1.21	1.24
480	2.5325	0.0295	1.16	
480	2.4728	0.0308	1.25	
500	2.5798	0.0718	2.78	
500	2.5785	0.0705	2.74	2.80
500	2.5811	0.0731	2.83	
500	2.5591	0.0731	2.86	

On substituting in place of the reaction tube used previously, which was bent round several times in the furnace, a straight tube with a bulb in the centre so that the total volume was the same namely 122 cubic centimetres, but whose inside area was only about one third that of the first, the following readings were obtained:

TABLE II

Temp. in °C.	Total HI in g.	HI decomposed in g.	Percent decomp.	Mean.
480	2.4606	0.0276	1.12	
480	2.3483	0.0263	1.12	1.13
480	2.3716	0.0271	1.14	
500	2.6286	0.0626	2.38	
500	2.6492	0.0614	2.32	2.38
500	2.6529	0.0651	2.45	

The general decrease in the percentage decomposition at both temperatures is significant suggesting that the effect is not due entirely to a purely gaseous reaction, since the volume of the reaction system was the same in the two cases. Since the surface has been decreased and the decomposition decreases accordingly, the extent of surface to some degree governs the reaction. That this apparent effect was real could be demonstrated more effectively by increasing many times, the difference in the extent of surface in the two cases. To effect this, glass powder was prepared as stated, which would pass through a fine sieve of approximately one square millimetre mesh, and was spread inside the reaction tube in such a way that the free space was now 100 cubic centimetres. Experiments were then made at temperatures of 400°, 460°, 480°, 500° and 520°C first with the empty tube and then with the tube containing glass powder, the duration of each run being twenty minutes. The decompositions so observed are given in Table III.

TABLE III

Temp. in °C	Total HI in g.	HI decomposed in g.	Percent decomp.	Mean.
400	2.21975	0.00825	0.371	
400	2.21942	0.00792	0.357	0.361
400	2.14162	0.00762	0.356	
460	2.7855	0.0210	0.75	
460	2.6956	0.0196	0.73	0.74
460	2.5625	0.0190	0.74	
480	2.4967	0.0327	1.31	
480	2.5325	0.0295	1.16	1.24
480	2.4728	0.0308	1.25	
500	2.5798	0.0718	2.78	
500	2.5785	0.0705	2.74	2.80
500	2.5591	0.0731	2.86	
520	2.5023	0.1578	6.31	
520	2.5508	0.1628	6.38	6.31
520	2.5243	0.1578	6.25	

The above are for the empty tube, the following for glass powder:

400	2.5770	0.0445	1.73	
400	2.5535	0.0435	1.71	1.73
400	2.3412	0.0412	1.76	
460	2.5905	0.1135	4.38	
460	2.5445	0.1115	4.38	4.38
460	2.5782	0.1127	4.37	
480	2.6013	0.1578	6.07	
480	2.5608	0.1503	5.87	5.95
480	2.5503	0.1503	5.90	
500	2.3804	0.1904	8.00	
500	2.5474	0.2029	7.96	7.98
500	2.4992	0.1992	7.97	
520	2.3866	0.2856	11.96	
520	2.3853	0.2843	11.92	11.94

The first point to notice, is the increase in the amount of decomposition at each of the temperatures in presence of glass powder over that in the empty tube. At 400°C the decomposition as calculated from velocity constants (see subsequent sections) is about five times as great, at 460°C seven and a half times, at 480°C, six times whilst at 500 and 520°C about four and five times respectively. It would consequently seem that the small effect of increased surface previously noticed has been fully confirmed. Further it would appear that, since the effect of surface decreases with increasing temperatures, the total decomposition measured is a complex quantity, one part of which was increasing more rapidly than the other. If we consider this complexity as being due in part to a purely gaseous reaction and in part to a reaction on the glass surface, the previous statement may be interpreted that the temperature coefficient of the gaseous decomposition of hydrogen iodide is greater than that of the surface reaction, and that whereas at 460°C the velocity of the gaseous reaction was seven times slower than that of the surface reaction, at 520°C it is only three times as slow.

Since the total amount of hydrogen iodide which passes in twenty minutes is known and also the volume of the tube in the furnace in each case, it is possible to calculate the time of contact of the gas with the hot tube, that is the actual duration of each experiment, and, from this, the velocity constant at each temperature both with and without glass powder. Table IV gives the results of such calculations with the logarithms of the velocity constants calculated in gram moles per litre per second.

TABLE IV

Reaction	Temp. in °C.	Velocity constant k	log k
Empty tube.	400	1.23×10^{-2}	−1.9112
	460	2.56×10^{-2}	−1.5918
	480	4.20×10^{-2}	−1.3768
	500	9.81×10^{-2}	−1.0083
	520	2.31×10^{-1}	−0.6364
Glass powder.	400	7.35×10^{-2}	−1.1339
	460	1.92×10^{-1}	−0.7167
	480	2.62×10^{-1}	−0.5817
	500	3.62×10^{-1}	−0.4413
	520	5.68×10^{-1}	−0.2457

If the logarithms of the velocity constants are plotted against the reciprocals of the absolute temperatures as shown in the figure it will be observed that straight lines are not obtained (Curves I and II). As previously assumed, the velocity constants observed are in all cases made up of a gas and a surface reaction. Since, however, the amount of gas reaction is very approximately the same in the two cases namely in the empty tube and with glass powder, the volumes of the reaction tubes being almost the same, if the velocity constants of the empty tube be subtracted from those with the glass powder the resulting values should be independent of gas reaction and the logarithms plotted against the reciprocal of absolute temperature should give a straight line. That such is the case is seen in Curve III shown in the figure. The slope of this line gives the heat of activation of the surface reaction and thence

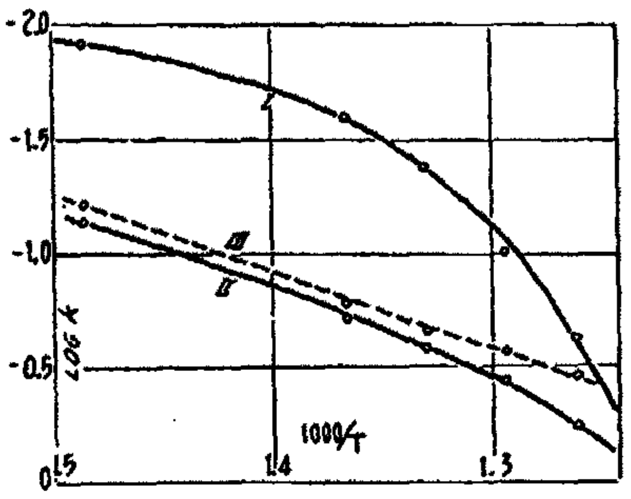

FIG. 1

Curve I, velocity of HI decomposition in empty tube.
Curve II, in presence of glass powder.
Curve III, velocity of surface reaction.

the temperature coefficient in the range studied. The value so obtained is 10,700 calories for the heat of activation, yielding a temperature coefficient for 10° in the region of 490°C of 1.10.

From the figures in Table IV it will be seen that for the data with glass powder the apparent temperature coefficient for 10° between 500 and 520°C is 1.22 whilst that between 400 and 460°C is 1.17 and the decrease would seem due to the increase in relative amount of surface reaction at the lower temperature. The value 1.10 obtained above would therefore appear to be a reasonable one in the limiting case of pure surface reaction.

In this connection it was of interest to find in an approximate manner what particular constituent in the glass was the effective catalyst. The possibility that during the early passage of hydrogen iodide through the tube, neutralisation might occur of some alkali in the surface layer, the influence of sodium iodide on the percentage decomposition of hydrogen iodide was studied in a manner similar to that used previously. It was found, however, that the resulting decomposition was comparable to that occurring in the empty tube. Using pure silica, however, which was powdered to the same extent as the glass employed above, the percentage decomposition at 480°C was 3.21, whilst with the glass powder at the same temperature 5.95 percent was decomposed and in the empty tube 1.24 percent. The catalytic effect of silica therefore is manifest. The greater influence of glass powder may be due to the fact that the silica in glass may assume the role of a promoted catalyst and, whilst the soda itself is inert, the possibility exists of its ability to promote the catalytic influence of the silica adjacent to it in the glass surface. On the other hand the effect may be simply due to differing surfaces in the glass and the silica.

As regards the purely gaseous reaction nothing can be said at present owing to lack of knowledge as to how the complex data above are to be divided. The straight line of surface reaction is of no assistance since the percentage of surface reaction at each temperature is not known. Suffice that, since from the curve the amount of gas reaction in the data for the empty tube, is rapidly increasing, the tangent to the curve at 520°C should give a very approximate measure of the temperature coefficient of the gaseous reaction. The value obtained is approximately 2. The value of the temperature coefficient obtained by Bodenstein, for what must have been a complex reaction comparable to that in the present experiments with the empty tube was 1.53 in the temperature region employed, that calculated from the data in Table IV between 500 and 520°C has exactly the same value.

However, even if it were possible so to divide the complex data actually observed into two parts namely a surface reaction and a gaseous reaction and from this division to calculate the absolute velocities of the two reactions, the evidence is not yet conclusive that the reaction velocity so calculated for the gaseous phase may be interpreted as relating solely to the gaseous bimolecular decomposition of hydrogen iodide. Further experiment may show that even this decomposition in the gas phase is a catalysed reaction and until such is proved incorrect the data even if available from a mode of treatment such as that above, may not be used for a strictly rigorous test of expressions for bimolecular gas reaction velocity.

Of the many so-called homogeneous gas reactions so far studied but one would appear to be truly so. The formation of phosphorus pentachloride as studied by the author recently (*loc. cit.*) is a true gas reaction being unaffected by the walls of the containing vessel as also by water vapour, but in this case, it was shown too that liquid chlorine and phosphorus trichloride react with violence even at −78°C, which would preclude the evaluation of the rate of combination.

With reference to the hydrogen bromide decomposition it would seem certain by analogy with the foregoing results that in this case also the glass surface of the reaction chamber would considerably affect the rate. It remains only for similar work as herein stated for hydrogen iodide to be repeated with hydrogen bromide to prove such a statement. The same should be true also of the synthesis of hydrogen bromide and iodide from their elementary constituents.

Summary

(1). The decomposition of hydrogen iodide has been studied by a dynamic method at temperatures from 400 to 520°C.

(2). The effect of a change in the extent of surface maintaining the volume of reactant constant, has been fully demonstrated, and the decomposition shown to be composite of a surface reaction and a reaction in the gas phase.

(3). The temperature coefficient of the surface reaction is 1.10 for 10° whilst that for the reaction in the gas phase would seem to be approximately 2 in the temperature range employed.

(4). The general bearing of such facts on the recent theoretical considerations of gas kinetics is indicated.

Princeton, N. J.

ADSORPTION BY ACTIVATED SUGAR CHARCOAL. III*

The Mechanics of Adsorption

BY F. E. BARTELL AND E. J. MILLER**

In earlier papers[1] we have shown that the process of adsorption of electrolytes, by activated sugar charcoal, from aqueous solutions is largely hydrolytic in nature. As a result of such adsorption an aqueous salt solution may become increasingly acidic or increasingly basic depending upon the nature of the salt used.

We have shown that the anomalous results obtained by previous investigators have, for the most part, been due to the presence of impurities in the charcoal used. Owing to the great differences in the nature of the results obtained by the earlier investigators it has not been possible to bring out a general theory covering the mechanics of adsorption which could be well supported by experimental facts. The results obtained by us were so surprisingly consistent that we felt justified in attempting to work out a generalization into which all our experimentally determined facts would fit, and from this develop a theory for the mechanics of adsorption of solutes by carbon.

The comparatively recent work on crystal structure, namely, the arrangement of atoms within a solid body, and consequently the arrangement of atoms thus necessary at the surfaces, as well as the excellent work on orientation of molecules at liquid surfaces, has been so well substantiated by recent experiments that the theories covering them are now regarded as practically established facts.

While Devaux was the first to make a careful study of oil films, Hardy[2] was probably the first to state clearly a theory of a definite orientation of molecules at a liquid surface. Langmuir's experimental data with layers of oil on water[3] has made it seem highly probable that definite molecular orientation of dissolved or partly dissolved (polar) molecules does exist at a water-air interface. Langmuir and Harkins, working independently, arrived at the same conclusion relative to the orientation of surface molecules. Harkins[4] states that, "The surface tension phenomena in general are dependent upon the orientation and packing of molecules in surface layers and the forces involved in that action are related to those involved in solution and adsorption." According to this view those substances containing so-called polar groups are more soluble than similar substances which do not contain these groups. According to this theory the active groups, such as COOH, CO, CN,

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*Presented at the New Haven meeting of the American Chemical Society, April 1923.

**Contribution from the Chemical Laboratories of the University of Michigan and Michigan Agricultural College Experiment Station.

[1] Bartell and Miller: J. Am. Chem. Soc., 44, 1866 (1922); 45, 1106 (1923).

[2] Hardy: Proc. Roy. Soc., 86 A, 610 (1912).

[3] Langmuir: J. Am. Chem. Soc., 38, 2221 (1916); 39, 1848 (1917).

[4] Harkins: J. Am. Chem. Soc., 39, 354 (1917); 39, 541 (1917).

OH or $CONH_2$ strive to enter the water and do so provided the other group is not too large. In case the other group is too large, it cannot be pulled into the water and a new phase must result. It is assumed that the soluble ends of the molecule (i.e., groups as above named) may still enter the water, and this results in a definite orientation of the molecules at the surface.

Our own experimental data on adsorption of solutes by carbon conforms well with the above view. With organic polar compounds concentration occurs at the surface and the molecules appear to become definitely oriented with radicals such as COOH, CO, CN, OH or $COHN_2$, pointing into the water phase with the hydrocarbon groups directly in contact with the solid carbon phase.

Theory of Mechanics of Adsorption. We shall accept the view presented by Langmuir that attractive forces ("residual forces") exist at the surface of all solids. These forces may be considered to be due to electronic behavior resulting in "stray fields" around the surface molecules. No attempt will be made to discuss this phase of the problem. We shall assume that these forces function as weak chemical forces in that different constituents of matter may be held upon the surface of the solid. These forces differ (possibly in magnitude only) from primary valence forces. It is through the operation of these residual forces that true adsorption occurs.

We shall postulate:

1. The characteristics of surface residual forces differ with different substances. The residual forces may operate so as to attract and hold anything which can be held by forces of that type and magnitude.

2. The residual forces may have preponderance of attraction for electropositive substances.

3. They may have a preponderance of attraction for electronegative substances.

4. There may exist a distribution of these residual forces such that they may exert equal attractive forces for electro-positive and electro-negative substances.

5. We shall accept the view expressed by Langmuir of definitely arranged condensation or adsorption points or "elementary spaces" existing upon the surface.

6. The work of Perrin,[1] Haber and Klemensiewicz,[2] Cameron and Oettinger[3] and others has shown quite conclusively that both H and OH ions impart to the surface a charge of the sign they carry. Perrin assumed the operation of some force holding these ions on the surface. Haber and Klemensiewicz consider that an adsorbed layer of water is held at the surface as a result of which the surface may function as a compound and reversible type of hydrogen and hydroxyl electrode. We shall accept this view, namely, that in the case of carbon in water or a water solution, H and OH ions are held on the surface, in a definite distribution arrangement.

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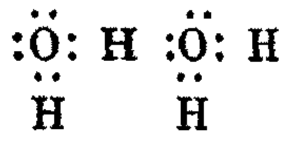
[1] Perrin: J. Chim. phys. 2, 601 (1904).

[2] Haber and Klemensiewicz: Z. physik. Chem. 67, 385 (1909).

[3] Cameron and Oettinger: Phil. Mag., 18, 586.

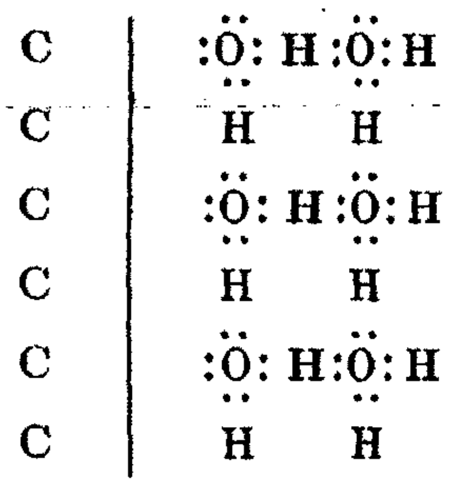
The effective covering of adsorption points by any given kind of ion is largely dependent upon the concentration of that ion in solution. Other ions may displace the H or OH ions held at the surface. Such displacement of ions results in so-called adsorption. Lewis[1] would indicate the electronic structure of water thus: $\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$. Each hydrogen atom has the same relation to oxygen and to the rest of the molecule. We can assume that water molecules are adsorbed on carbon and that the apparent ion adsorption is dependent upon a change of intensity with which the different atoms are held together by the electron pairs.

Accepting the Lewis theory for sharing of electrons, water molecules are held together as follows:



$$:\underset{\substack{\cdot\cdot\\ \mathrm{H}}}{\overset{\cdot\cdot}{\mathrm{O}}}:\ \mathrm{H}\ :\underset{\substack{\cdot\cdot\\ \mathrm{H}}}{\overset{\cdot\cdot}{\mathrm{O}}}:\ \mathrm{H}$$

The orientation of the adsorbed film might be considered thus:



Inasmuch as we have no definite proof relative to the precise orientation of adsorbed water molecules we shall use the simple diagram below.

$\mathrm{C{-}H}\qquad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\ \mathrm{H}$ (H ion adsorption)

$\mathrm{C{-}H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\qquad \mathrm{H}$ (OH ion adsorption)

$\mathrm{C{-}H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$ (Molecular H_2O adsorption, greatly in preponderance)

A view, similar in some respects, has been expressed by Mukherjee[2] who states: "We shall assume that the atoms on the surface do not exert any chemical affinity on the hydrogen and hydroxyl ions as such, or on the dissolved acid with which it may be in contact. The adsorbed water molecules behave as a solid layer, being held by strong chemical forces. It is clear that the surface will be neutral in contact with chemically pure water. The mole-

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[1] "Valence and Structure of Atoms and Molecules," Chem. Cat. Co. 1923.

[2] Phil. Mag. (6) 44, 321 (1922). The main points of difference between the views of Mukherjee and our own are that we assume that atoms on the surface may exert a "chemical affinity" on hydrogen and hydroxyl ions as such during the periods these ions are dissociated as above indicated. This period may be of extremely short duration and the degree of dissociation of the water molecules at this surface is probably of about the same order as the degree of dissociation of the molecules in the bulk of the liquid-water. We assume further that the surface may not be neutral in contact with pure water but instead that the surface forces of the adsorbent may be of such a nature as to bring about a tendency to share electrons such that either a preponderance of H or of OH ions may be held on the solid surface while the ion of opposite sign resides in the adjacent liquid layer; this would tend to give an apparent electrical charge to the solid. We assume that an adsorbed ion is directly in contact with the adsorbent.

cules of water in the adsorbed layer are in thermodynamic equilibrium with those in the bulk of the liquid. It is reasonable to suppose that a transfer of an electron is taking place between the hydrogen atom and the hydroxyl group in the water molecules in the surface layer, as it does in the molecules in the liquid since the adsorbed water molecules behave as a solid layer, recombination would take place mostly between adjacent hydrogen and hydroxyl ions. The recombination will be extremely rapid. It can be assumed that at any instant the number of hydrogen or hydroxyl ions actually remaining free in the surface will be a negligible fraction of the total number of water molecules."

7. Other ions may displace the H or OH ions thus held at the suface. Such displacement of ions results in so-called adsorption.

8. In case one ion is replaced by another, the dissociation tendency for that ion with its associate ion may be greater or may be less than the dissociation tendency for the pair previously held. This would result in an opening or closing of their electrical field and would result in a change in the magnitude of the double electrical layer potential. The double layer charge of the particle may be due to this effect. True adsorption in aqueous solutions is probably, in the majority of cases, of this type.

Mechanics of Adsorption. We may consider the following as representing equilibrium conditions of the system, carbon-water:

$$\text{(a)}\quad C.H_s^+ - OH_f^-$$
$$\text{(b)}\quad C.HO_s^- - H_f^+$$
$$\text{(c)}\quad C.HOH_s \quad \text{(greatly preponderant)}$$

C. represents carbon adsorptive capacity.

H_s^+ and OH_s^- represent adsorbed ions.

H_f^+ and OH_f^- represent "free ions" in liquid layer (outer electrical layer).

Let the solute in solution give $MA = M^+ + A^-$. Consider first the effect upon condition (a).

$C.H_s^+ - OH_f^- + M_f^+ + A_f^-$. If MA is highly dissociated and if M^+ does not displace H_s^+ the equilibrium change will be negligible. If on the other hand M^+ does displace H_s^+, the equilibrium of this system may be represented, first as:

$$\begin{array}{l} C.\quad OH_s^- - H_f^+ \\ C.\quad H_s^+ - OH_f^- + M_f^+ + A_f^- \\ C.\quad OH_s^- - H_f^+ \end{array}$$

and after adsorption as:

$$\begin{array}{l} C.\quad OH_s^- - H_f^+ \\ C.\quad M_s^+ - OH_f^- + H_f^+ + A_f^- \\ C.\quad OH_s^- - H_f^+ \end{array}$$

M_s^+ has displaced H_s^+. We may consider that MOH has been adsorbed and we have our choice of considering whether M_s^+ is in equilibrium with OH_s^- or OH_f^- or both, (i.e., whether the OH ion of MOH is itself actually adsorbed). For convenience we shall indicate the equilibrium as follows:

$$\text{(d)}\quad C.M_s^+ - OH_f^-, \text{ or, } CM_s^+ - A_f^-$$

depending upon the chemical affinities and resulting equilibrium conditions between M^+ and A^- and OH^-. With this view it is possible to see why an anion may wander off into solution. It lies of course at all times near an associate of cation, in the above case the H ion. Likewise, we must consider condition (b) $C.HO_s^- - H_f^+$. If A_f^- does not displace HO_s^- the effect will be but slight. If A_f^- does displace HO_s^-, then we will have:

(e) $C.A_s^- - H_f^+$ (or, $C.A_s^- - M_f^+$)

Both H_s^+ and OH_s^- might be displaced which would result as follows:

(f) $C.M_s^+ - OH_f^-$

(g) $C.A_s^- - H_f^+$

We see that the equilibria at (f) and at (g) may be largely independent of each other. The velocity of the displacement reactions may be far different.

The Sign of the Particle

The apparent charge upon the solid and the resulting magnitude of the electrical double layer is dependent upon the dissociation tendency of the substances adsorbed. Consider M^+ and A^- equally adsorbed, then if dissociation in (f) is greater than that in (g) the particle will appear positively charged even though the actual adsorption of M^+ and A^- are the same. Addition of acid tends to repress the dissociation represented in (b); likewise tends to increase the adsorption of H_s^+ in (a). Addition of base represses dissociation represented in (a) and increases adsorption of OH^- in (b). In so far as ionization tendencies of molecules, that is, of ion pairs, are concerned, those adsorbed respond in the same general manner to ion concentration changes as do those within the liquid phase. We can show further that the Freundlich adsorption formulation $x/m = \alpha C^{1/n}$ should apply.

On considering the adsorption of the individual ions the adsorption isotherms for the cations M, and anions A, can be expressed:

$$\frac{XM}{m} = \alpha M_1 C \beta M$$

and

$$\frac{XA}{m} = \alpha A_1 C \beta A$$

α M and β M values, according to Svedberg[1], might be quite different from the α A and β A values.

Replacement Effects of Ions with Carbon as Adsorbent

On the basis of the above theory—a determination of the OH ion concentration of solutions of different salts with a common cation before and after adsorption should give an indication of the relative adsorption of the different anions, the adsorption being determined by the amount of OH ion set free. Based upon this test we obtained the oder for relative adsorption of anions by carbon.[2] While these determinations were not made with a high degree of accuracy, they did, however represent fairly accurate qualitative results. It was noted that we obtained an adsorption order quite similar to the Hofmeister series.

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[1] Svedberg: Report of Faraday Society and the Physical Soc. of London, p. 2 (1920).

[2] Bartell and Miller: Loc. cit.

On the whole it was found that negative radicals with hydrocarbon groups displaced OH more readily than did the inorganic radicals. All negative radicals were able to displace OH^- at least to some extent from carbon. Ions of metals less noble than H did not displace H^+ from carbon. Metals[1] more noble than H did displace H^+. A salt in solution having a cation less noble than H when treated with carbon gave an alkaline reaction. The reactions may be represented as follows: Let mA = Salt with cation less noble than H.

$$\begin{array}{lll} \text{(h)} & C.H_s^+ - OH_f^- \quad + m_f^+ + A_f^- = & C.H_s^+ - OH^- + m_f^+ - OH_f^- \\ & C.HO_s^- - H_f & C.A_s \quad H^+ \end{array}$$

A salt in solution having a cation more noble than H will give an acid reaction.

$$\begin{array}{lll} \text{(i)} & C.H_s^+ - OH_f^- + M^+ + A^- = & C-M_s^+ - OH_f^- + H_f^+ + A_f^- \\ & C.HO_s^- \quad H_f^+ & C-HO_s^- - H_f^+ \quad \text{also,} \\ & & C.M_s^+ - OH_f^- + HOH \\ & & C.A_s^- - H_f^+ \quad (H_f^+ + A_f^-) \end{array}$$

Some A^- will be adsorbed, but relatively less A^- will be adsorbed than M^+; therefore the reaction of the solution will be acid. Salts with hydrocarbon cations behave as noble metals in displacement of H^+ from carbon. A conclusion somewhat similar to the above was reached by Tammann[2] who measured potentials of minerals galena, litharge, zinc blende, graphite, magnetite, Iron pyrites, etc., against a normal hydrogen electrode. He studied these minerals under different conditions of polarization in contact with solutions of their salts and found that less noble cations were exchanged for the more noble hydrogen cation. This H cation then protected them from exchange with metal ions which were less noble than H ion. This work was believed to substantiate the observations of Rubens[1] and to explain the adsorption of very small quantities of radio active substances and of small quantities of noble metals in compounds of the less noble metals.

Adsorption of Acid Dyes by Carbon

Consider an acid dye, such as sodium picrate, to be of the general type $mR_A = m^+ + R_A^-$

The solution containing activated carbon becomes alkaline with the first addition of a dilute solution of dye. We have here conditions as in (h). R^- displaces OH_s^- and is adsorbed, liberating OH^- ion to solution. The m^+OH^- liberated to the solution accounts for the alkaline reaction. With successive additions of dye solution the replacement of OH_s^- becomes less and less so that successive additions of dye throws successively less OH_s ion into solution. No H_s ions are displaced by m_f^+.

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[1] We have evidence that some polyvalent cations less noble than H as Fe^{+++} can displace H. In practically every case in which H has thus been displaced, the displacing ion has been reduced. For example, Fe^{+++} was reduced to Fe^{++}. Ions of the noble metals are reduced to free metal as Ag^+ to free Ag.

[2] Z. anorg. Chem. 113, 149-62 (1920)

Basic Dyes

As a general type we may take $R_cA = R_{cf}^{+} + \bar{A}$ (i.e., methylene blue).

The reaction in this case progresses according to (i) above. The cation readily displaces the H_s^+ from carbon and the rate of reaction is rapid. The anion can displace OH_s^- from carbon, but the reaction is less rapid and the displacing power is less than that of the cation Rc_f^+ with the following result. Upon addition of carbon to a solution with low concentration of dyestuff, the solution will become distinctly acid, but as adsorption of anion progresses the solution will become less acid and finally will again be left neutral. At higher concentration of dyestuff or addition of larger amounts of it, the adsorption of A^- will reach practically its maximum while R_c^+ continues to be adsorbed. This liberates H^+ to the solution giving permanent acidity and the system behaves in every way according to type (1). As more RA is added to the solution R_c^+ adsorption continues and the color is removed until the displacement of H_s^+ by R_{cf}^+ reaches a maximum.

Adsorption vs. Chemical Constitution

According to the foregoing view it is seen that adsorption demands orientation of molecules at surfaces. Furthermore, in case the molecules are polar and contain COOH, CN, OH, Cl, or $CONH_2$, etc., these groups would extend toward the water phase, in fact would probably exist in the outer double electrical layer. The addition of one or more of these groups to a molecule would tend to make it more polar, accordingly more soluble, with the result that the positive ion would tend to pass to the solution and less of it would be adsorbed for a given concentration. This we have seen to be the case. It has been found that benzoic acid is highly adsorbed, according to the above view we must consider the negative radical is in this case in contact with the carbon. The addition of an hydroxy group to this compound decreased the amount adsorbed. The addition of the hydroxy group to succinic acid likewise decreased the adsorption, while the addition of the second hydroxyl group decreased the adsorption still more. The introduction of an amino group decreased the adsorption even more than the hydroxy group. Similar results were obtained when the hydroxy group was introduced into propionic acid. Introducing CH_2 groups into the anion increased its adsorption. This has been observed also by numerous investigators. The benzene ring structure likewise results in higher adsorption. We may consider then that an increase in hydrocarbon content results in a decreased solubility in water, at the same time it is probable there results an increase in affinity for the carbon. According to the above we can see that organic, i.e., carbon containing radicals are readily adsorbed. They may displace either H^+ or OH^- depending upon their charge.

Inorganic acids are but comparatively slightly adsorbed because the inorganic anion replaces more feebly the OH_s^- ion. Inorganic bases are adsorbed scarcely at all, owing to the fact that cations of metals less noble than H do not displace H^+ from carbon. Thus we have no concentration of base at the interface.

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[1] Sitzungsber. Akad. Wiss. Berlin 1, 47 (1917)

Summary

The facts from our experimental data are in accord with the following theory:

1. The surface structure of activated sugar charcoal has a crystal lattice such that the surface atoms form "elementary spaces" from which operate residual forces. The nature of these forces are such that in water solution H and OH ions are held adsorbed in a more or less definite and regular arrangement.

2. The OH ions thus held can be displaced by almost any anion and are most readily displaced by organic anions.

3. The H ions thus held can be displaced to any appreciable extent' only by cations more noble than H. (Also by cations with a valence greater than two).

4. Radicals containing hydrocarbon groups readily displace either H or OH ions. The longer a hydrocarbon chain the greater the displacement i.e., the greater the adsorption.

5. Adsorbed molecules of solute are oriented at the solid liquid interface, the more polar portion being on the solution side, the less polar in contact with the carbon.

6. The addition of COOH, OH, or $CONH_2$ group to an organic acid causes the latter to become more highly polar with the result that the solute tends to be drawn to the solution phase bringing about a lesser concentration of solute at the interface with an attendant lesser adsorption. This statement holds good only for adsorption from water solution. Entirely different results might be obtained with an organic solution.

7. The introduction of a second carboxyl or hydroxyl group results in an increased polarity, a decrease in adsorption, and a decrease in concentration at the interface.

8. With a basic dye, the molecule is oriented at the surface so that the positive dye radical is in contact with the carbon. In the case of methylene blue the dye radical is held adsorbed by the carbon having displaced H ion, and the Cl radical of the dye displaces OH ion, though to a lesser degree, and is also adsorbed. The velocity of the latter displacement is much lower than that of the first, which results in temporary acidity of solution which gradually disappears.

9. With an acid dye such as sodium picrate, the dye radical readily displaces the OH ion causing the solution to become alkaline. The sodium ion being less noble than H ion cannot displace that ion from carbon, with the result that the solution remains alkaline.

10. Orientation of molecules due to adsorption will result in the formation of an electrical double layer, this layer occurring between the adsorbed ion and its associated ion of different electrical sign which is opposite it in the liquid layer. The magnitude of the potential of this electrical double layer

will be largely dependent upon (a) the degree of adsorption of the one ion and (b) the tendency of the ion pair to dissociate. Such ion pairs are never widely separated but each aids in forming the effective surfaces of the electrical double layer.

11. Our data have shown that in the case of carbon with the various solutes investigated, the order of adsorption or increase in concentration at the interface is in general agreement with the change in surface tension at an air-liquid interface. This fact shows that the extent of change of surface energy in both cases is similar and that we must consider decrease in free surface energy in connection with adsorption studies.

NEW BOOKS

Protoplasmic Action and Nervous Action. *By Ralph S. Lillie. 19×13 cm; pp. xiii+417. Chicago: The University of Chicago Press, 1923. Price: $3.00.* In the preface, p. xi, the author says: "The general physical conditions under which chemical reactions are initiated, accelerated or retarded, and influence other reactions at a distance are undoubtedly the same in living as in non-living matter; but the special features of composition and arrangement in the protoplasmic system often render detailed analysis difficult. Under these circumstances the study of "models"—simple artificial systems in which the action of single factors may be isolated and observed—may be of great service, and I have made use of this method in a number of instances. For example, the transmission of the effects of stimulation in nerve and other irritable forms of protoplasm resembles closely certain types of chemical transmission or distance-action in metal-electrolyte combinations; many biocatalytic reactions are identical with those induced by colloidal platinum or charcoal; there are also instructive analogies between organic growth and certain types of inorganic growth. Many fundamental physical processes which play an important part in protoplasm are independent of the special chemical composition of the material; thus the influence of radiation and electricity on living matter is a special case of the general influence which these agents exercise under appropriate conditions upon all chemical reactions. The detailed nature of the conditions in protoplasm can be determined only by special investigation."

The chapters are entitled: general characteristics of living matter; the cellular organization of living matter; general characters of living organisms; general peculiarities of protoplasm as a physical system; physical nature of protoplasmic structure; protoplasmic structure; general conditions determining the properties of protoplasmic membranes; relation of the inorganic salts of the medium to the physiological processes in protoplasm; general physiological action of lipoid-alterant and surface-active substances; catalysis in relation to the chemical processes in living matter; electrical and other factors in the catalytic action of protoplasm; stimulation and transmission of excitation in protoplasm; bioelectric phenomena; membrane changes during stimulation; the physico-chemical basis of transmission in nerve and other protoplasmic systems.

"There is also evidence that the internal protoplasm of the single cell is frequently pervaded by a system of films or closed partitions giving a chambered type of structure; and the possibility of intracellular chemical differentiation ("chemical organization") has been referred to this condition. Such a chambered structure corresponds essentially to that of an emulsion-like or alveolar system. Apparently any physico-chemical system which is built up largely of water and substances in aqueous solution must be a partitioned system if it is to maintain within a small space a high degree of chemical differentiation together with a corresponding diversity of chemical activity," p. 22.

"In all organisms this selection of assimilable material from the environment and its transformation into living protoplasm proceed automatically and are regulated in correspondence with the physiological requirements, as these vary with the changes of activity and of external conditions. Both the automaticity and the regulated character of these activities are well illustrated by the changes in the reaction of animals to food materials during periods of "hunger." Consumption of the energy-yielding reserves within the living protoplasm leads to an increased reactivity of the whole organism to these substances. Through this means the maintenance of the metabolic equilibrium is assured under the usual conditions. Regulation of this kind is shown to a greater or less degree by all organisms, and constitutes a fundamental condition of self-preservation; typically if the organism is deprived of any substance or condition necessary for maintenance, its reactivity and behavior are altered in a manner tending to compensate or remove the deficiency. Thus hunger is, physiologically speaking, increased reactivity to food materials; thirst is increased reactivity to water; the respiratory center of vertebrates increases its rhythm as CO$_2$

accumulates in the blood; when the oxygen in the water is decreased, the gill-cilia of the fresh-water clam beat more vigorously. These and many other instances illustrate the manner in which a physiological deficiency may itself furnish the means of setting in motion some physiological mechanism which remedies the deficiency. The end-effect of all such regulatory responses is to further the persistence of the organism in its environment. As already mentioned the term *adaptive* is usually applied to those special peculiarities of structure and activity by which the organism is automatically conserved in spite of environmental change; hence, from the present generalized point of view any active adaptation may be regarded as a special kind of regulation. It is evident that all such regulations are based upon a highly developed irritability; this fundamental property of irritability, therefore, controls all of the active relations between organism and environment, including the interchange of material and energy which is the essential feature of such relations," p. 29.

"The general conclusion seems therefore justified that the specific biological characters of an animal or plant depend ultimately upon the specific chemical characters of its proteins. The developing germ, or the growing and metabolizing organism, builds up proteins of specific constitution, and these, since they determine the specific structural characters —with the correlative physiological activities—or the organism, form the basis of its biological specificity or special singularity as an organic species. A fundamental problem, therefore, relates to the condition determining the synthesis of proteins of its own specific type by each form of protoplasm. This problem is as yet unsolved. Apparently the presence of proteins of a certain composition and configuration promotes or "catalyzes" the formation of proteins of similar or complementary configuration. A general condition comparable with autocatalysis thus determines the specific character of the protoplasmic syntheses, but such a statement merely defines the problem without solving it. The problem, however, cannot be solved before it is clearly defined, and its solution would unquestionably represent a great advance in biological knowledge, since it would involve the solution of the fundamental problems of growth and heredity," p. 36.

"The experimental studies and observations of the last twenty years have led more and more to the conclusion that the general or fundamental structure of protoplasm corresponds more closely to that of an emulsion than to that of any other simple non-living physical system. The most general facts of its chemical composition are in agreement with this conclusion. Water-insoluble constituents (lipoids) occur in association with colloidal constituents which have water-combining powers (proteins). The whole resulting complex is during life immiscible with water, and typically is bounded from the external watery medium forming its immediate environment by a layer or surface-film having semi-permeable properties. The semi-permeability and the water-immiscibility of the surface layer appear to be interdependent properties; they suggest the existence of a continuous external layer of water-insoluble material of fatty or similar nature. The unit of organic structure, the cell, would thus appear to be a system with an aqueous internal phase limited externally by a thin water-insoluble phase or boundary layer. The aqueous internal phase forms one component of a system, the cell protoplasm, which is structurally and chemically highly complex, and emulsion-like in its general physical constitution," p. 67.

"Höber and Kozawa found this isoelectric point to vary for different species of corpuscles and to be characteristic for a particular species; i.e., certain corpuscles are more readily made positive than others by H ions and polyvalent ions; thus the corpuscles of rabbits and guinea pigs were found to require the least H-ion concentration for reversal and those of the ox and the pig the highest; those of the dog, cat, goat, and man were intermediate," p. 100.

Graham observed in 1854, p. 148, that "potassium sulphate showed positive osmosis in alkaline solution and negative in acid when a bladder membrane was used; sodium chloride, on the contrary, showed positive osmosis in acid solution and was indifferent in neutral solution. . . . The transport of the ions of salts, and consequently the permeability of a given membrane to a diffusing salt, are similarly affected by the electrical state of the partition, and this influence has recently been studied by Girard. If the polarization of the membrane (potential difference between its opposite faces) has certain orientation, the penetration of a salt like magnesium chloride or sodium sulphate in the one direction is facilitated, in the other direction hindered."

"If during the local stimulation-process there is in fact a temporary breakdown or dissolution of the protoplasmic surface film, a temporary increase of permeability to water-soluble diffusible substances should be associated with stimulation. The normal semi-permeability of the living cell, implying impermeability to water-soluble substances of low molecular weight (neutral salts, sugars, and amino-acids), depends on the structural continuity of the plasma membrane; and when this continuity is interrupted in any way, the effect is equivalent to a loss of semi-permeability. Such an effect may be temporary and difficult to detect in those cases where the surface-film is rapidly re-formed; but in the more favorable instances we should expect to find direct evidence of increased permeability during stimulation, in addition to the indirect indications afforded by the bioelectric variation and the refractory period," p. 346.

"Direct proof of the increased permeability of rapidly responding tissues like vertebrate muscle or nerve during normal stimulation is difficult to obtain. In the case of muscle the results gained with the method of electrical conductivity are of uncertain value, since the change in the form of the tissue, the production of electrolytes (e.g., lactic acid) in the process itself, and the change in the distribution or quantity of the intercellular fluids (lymph), all affect the total conductivity; hence the observed alterations may depend on other factors than the changing permeability of the plasma membranes. Direct observation of the penetration of easily detectable compounds into the muscle cell has given better results; recently Mitchell and his associates have shown that rubidium and caesium chlorides do not enter the muscle cells when the resting muscle is perfused with Ringer's solution containing these salts, but penetrate readily when the tissue is thrown into contraction by stimulating the nerve. In this case there seems to be an unequivocal demonstration of increased permeability to inorganic salts during stimulation. Embden finds that frogs' muscle gives off inorganic phosphate to the medium during contraction but not during rest, and he regards this fact as further evidence of an increase of permeability during stimulation, "p. 356.

"The general fact that chemical effects are produced in protoplasm by the electric current and that protoplasm produces electric currents in its activity, when considered in conjunction with the further fact that these phenomena are dependent on the structure of the living system and disappear with the loss of semi-permeability (as at death)—as well as the various other facts reviewed above, which relate stimulation to membrane changes—indicates clearly that the electrical sensitivity of living protoplasm is intimately connected with the presence of the semi-permeable partitions or surface-films. These partitions have high electrical resistance and are therefore highly polarizable; they are also extremely thin; hence when they are polarized by the passage of a current there is a correspondingly steep fall of potential between their opposite faces. The hypothesis naturally suggests itself that the existence of these steep gradients is the essential condition on which the chemical action of the electric current in living protplasm depends," p.406.

"Such a conception of protoplasmic structure and action is fully consistent with the views reached on the basis of histological research, and it has the further advantage of correlating the structural features of the living system with the special peculiarities of its chemical and physiological behavior. The great diversity exhibited by living organisms shows that the protoplasmic type of constitution permits the widest variation in the details of structure and activity. Yet the essential or fundamental structure common to all forms of protoplasm is apparently uniform; viz., a film-partitioned or film-bounded arrangement or organization of phases of different chemical composition. With this type of structure, of which an elementary model is an emulsion structure, the properties of growth, chemical activity, and irritability characteristic of living matter appear to be intimately bound up. Systems having this structure will give a maximum of polarization when traversed by electric currents, and hence a maximum of chemical effect. Most of the problems relating to the mode of action of such systems, especially the problem of the conditions of specific synthesis (the most characteristic property of living matter), are still unsolved. The study of artificial systems having a similar type of physical constitution may be expected to throw further light on the nature of protoplasmic action, and also to indicate the directions in which further physiological research is most desirable," p. 409.

Wilder D. Bancroft

Physikalisch-chemische Übungen. *By W. A. Roth. Third edition. 22×15 cm; pp. viii+278. Leipzig: Leopold Voss. Price: Seven shillings.* The present edition of this well-known work on practical physical chemistry was published in 1921, and is a photomechanical reproduction of the second edition, purged of its errors, with various supplementary sections added at the end of the book. This method of taking account of new material has, of course, a number of disadvantages, but was probably justified by existing high production costs which would have entailed an increase of price if the book had been entirely re-set.

On the whole, the book is very good and is doubtless widely used, as it deserves to be, in German laboratories. The whole range of physical chemistry is covered, and the experiments and apparatus are clearly discussed and explained. The diagrams and illustrations of apparatus are, however, in most cases distinctly inferior. Emphasis is laid on the importance of fully understanding the calculation of results from experimental data, and many specimen calculations are given. In the supplementary sections, titration by conductivity measurements, hydrogen electrodes, freezing-points of metallic alloys, and colloids, are among the most important subjects discussed.

Since all German students doubtless have at hand, for reference, the larger books by Ostwald-Luther-Drucker and by K. Arndt, one cannot help thinking that the author would improve his book as a text-book for students, by omitting many of the more purely physical exercises, which are usually carried out in a physics laboratory, and some of the qualitative experiments and theoretical discussions, which appear to belong, more appropriately, to a text-book dealing with the theory of the subject. In this way, the cost of the book would be reduced or, alternatively, room would be made for further experiments of physical chemical interest.

Alex. Findlay

Introduction to Physical Chemistry. *By Sir James Walker. Ninth edition. 21×14 cm; pp. xii+438. New York: Macmillan and Co., 1922. Price: $4.50.* This has been one of the standard text-books for a quarter of a century. In the preface to this edition the author says that it has been found necessary to revise many chapters and practically to rewrite those dealing with the intimate nature of the atom and the system of the elements.

The reviewer was much interested in the graph, p. 27, for the relation between atomic weight and specific heat, also in the paragraph, p. 68. 'Occasionally it happens in the practice of organic chemistry that a substance, whose nature is unknown, is suspected, on account of similarity of melting-point to be identical with a given substance. In such a case the known and unknown substances are mixed and a 'mixed melting point' is taken. If the substances are identical, the melting point remains unchanged. If they are different, the melting point is lower and no longer sharp, as each of the mutually soluble organic substances lowers the melting point of the other."

On p. 61 the author says that "the occurrence of an absorption band in the spectrum of a compound is often attributed to a manifestation of 'residual affinity' existing in the molecule. Fully saturated organic compounds show no banded absorption, but compounds containing 'double bonds', or atoms such as those of oxygen or nitrogen, which are capable of assuming a higher valency than is associated with them in the ordinary formulation, frequently display well-marked absorption spectra. Here 'residual affinities' and 'partial valencies' come into play which are not expressed in the ordinary organic constitutional formulae."

"Water and alcohol yield brown solutions with iodine and may therefore be reasonably supposed to form some species of compound with the iodine, as there is no evidence of dissociation of iodine molecules. If iodine is dissolved in glacial acetic acid at the ordinary temperature, the solution is brown; but, when the solution is heated to the boiling point of the acid, it assumes a distinctly pink colour. This behaviour may be held to indicate that the compound of iodine with acetic acid, stable at the ordinary temperature, decomposes when heated to the vicinity of 100°," p. 219.

"Considerable light has been thrown on the structure and magnitude of colloidal particles by means of X-ray analysis. It will be shown that a homogeneous beam of X-rays may be applied to elucidate the internal structure of a crystal. By an ingenious modification the method may be applied, not to a single definitely-oriented crystal, but to a rod of compressed crystalline particles of every possible orientation. By measurement of the lines obtained on a photographic film, conclusions may be drawn both as to the structure of the crystals, and as to the size of the crystalline particles. Liquids and truly amorphous solids, *e.g.* glass, give none of the characteristic lines of crystals. Investigation showed that the particles of colloid gold protected by gelatin and evaporated to dryness are in reality crystalline, and that they possess the same structure as that of massive gold crystals. The values for the magnitudes of the colloidal particles of gold agreed closely with those obtained by other methods. Colloidal silicic acid appeared to be mostly amorphous but contained many crystalline particles. Gelatin was completely amorphous," p. 228.

It seems a pity to tell the student, p. 178, that "the osmotic pressure of a substance in dilute solution is numerically equal to the gaseous pressure which the substance would exert were it contained as a gas in the same volume as is occupied by the solutions." It would be much better to say, as van't Hoff did, that the volume in question is that occupied by the solvent; but that this is practically the same as the volume occupied by the solution in the case of a dilute solution.

The author seems to believe in Ghosh's figures, p. 262, and he writes the formula for mercurous chloride as HgCl instead of Hg_2Cl_2, p. 347. Both these points should be changed in the tenth edition.

Wilder D. Bancroft

Thermochimie. *By F. Bourion. (Collection de physique et chimie, issued under the direction of P. Langevin, J. Perrin and G. Urbain).pp. xii+363. Paris: O. Doin, 1924. Price: 25 francs.* There is a need at the present time for a treatise on thermochemistry in which the experimental methods used, and the results obtained, since the publication of the classical treatises of Berthelot and Thomsen are described. The advances in technique and the somewhat drastic revision of some of the earlier results are not sufficiently described in the treatises on physical chemistry, and the literature is very diffuse. In bringing together some of the newer researches, and discussing some of the results, the author of the present work has performed a useful service, and his book may be welcomed as an addition to the library of the chemist. In some parts, as will be explained below, it is far from giving a true picture of the present state of the subject, and the absence of an index removes most of its value as a work of reference. One of the most regrettable features of the majority of French books is the absence of an index, and there is no doubt that their use by the English and American reader is seriously restricted by this omission. The editors of a new series of treatises, such as the one at present discussed, would do well, if they hope to reach a larger circle of readers, seriously to consider this question.

The subject of thermochemistry can hardly be studied with advantage apart from the science of thermodynamics, of which it forms a part, but it is a convenience to have a separate work on the experimental side of the subject. Many of the more accurate values of the thermal magnitudes have been determined by indirect methods, and the present treatise gives a full account of these methods, with ample illustrative examples.

The book begins by a brief description of the theory of heats of reaction, and of their variation with temperature (law of Kirchhoff). It is pointed out that an exact knowledge of a heat of reaction involves also an exact knowledge of the specific heats of all the substances taking part in the reaction, and also of the latent heats of any changes of state which may occur. A description of direct calorimetric methods then follows, in which attention is paid to the various methods of determining the cooling correction. It is stated that the book is based on original memoirs, and it is therefore to be regretted that so many names in this and other sections are given incorrectly. The experiments at high and low temperatures are considered, and an excellent description is given of the method applied in the determination of the heats of reactions which occur slowly, such as the inversion of sugar.

The section dealing with the determination of the latent heats of fusion and of evaporation is less satisfactory. Only a few methods are described, and in the case of latent heats of evaporation the method of Berthelot is given without an indication that it is far from satisfactory. This method was made the object of a careful study by Harker, and the errors in it are known to be large.

A good account of the determinations of the specific heats of solids at low temperatures made by Nernst and his school is given. The numerical details quoted add greatly to the value of this section.

The short section devoted to the specific heats of gases is extremely unsatisfactory. None of the newer methods is even mentioned, and the information supplied gives a completely erroneous impression of the actual state of the subject. Of direct methods, only those of Regnault, of Mallard and Le Chatelier, and of Langen are given. All these have long been superseded. Clement and Desormes' method only is mentioned among those depending on adiabatic expansion, and Kundt's method only among those utilizing the velocity of sound. The author states (p. 359) that the text-book of Nernst was among the treatises consulted; it is much to be regretted that he did not make more extensive use of the information on the recent work on the specific heats of gases which is contained in it. The slightest thought cannot fail to bring home the great importance of a knowledge of the specific heats of gases in nearly every branch of chemical technology. There is no point in determining with any accuracy the thermal values of fuels if the thermal capacities of the gases leaving the flues is not known with an accuracy within 25 per cent., yet something of this kind is the general practice among engineers. The numerical results given on pp. 124-125 are far from accurate. It is also incorrect to class hydrogen among other diatomic gases (O_2, N_2, HCl, CO, NO) as having a value of C_V approximately 5 cals.; the specific heat of hydrogen is abnormally low.

A clear account, with examples, is given of the various methods used in the indirect determination of heats of reaction. These nearly all depend on the application of the Second Law of Thermodynamics, and the author confines himself to the formulae as given, and shows how they can be applied. It is clear that modern thermochemistry is becoming more and more a branch of applied thermodynamics, and that results obtained by the aid of the Second Law are in many cases more accurate than those found by direct methods. The values of the fundamental constants (*e.g.* R) used differ in various parts of the book.

The second half of the book is taken up by a discussion of "*Relations stoechiométriques en thermochimie.*" The idea that the heat of reaction is a measure of the affinity of a reaction has long ago been abandoned, but a large number of generalisations of great value in this field are known. Thus, the fact that the heat of neutralisation of a strong acid by a strong base is constant (the recent work of Richards and Rowe is not mentioned) leads to conclusions as to the state of solutions. The determination of the partition of a base between two acids by the method of Thomsen, the law of thermo-neutrality, and the phenomena of hydrolysis, are all described in detail. The method of Urbain, Job and Chauvenet for the detection of complexes in solution is considered. Variable volumes of solutions of salts are mixed in such a way that the total volume, corresponding with a total unit molecular concentration, is constant, and the evolutions of heat are plotted against composition in the same way as in the freezing point diagrams. Maxima and minima occur in positions corresponding with double or complex salts.

The concluding section deals with the difficult field of thermal phenomena as related to constitution among carbon compounds. It is emphasised that the experimental results are still not sufficiently accurate to enable one to proceed to any very satisfactory systematic considerations in this field, although some interesting conclusions may be reached, for example, in substitution when the exalting and depressing actions of certain groups are studied. The most recent value for the heat of combustion of benzene (781-7 cal.) favours the Ladenburg or centric formulae according to the method of calculation of Thomsen, which requires 9 single linkages, yet when the formula for the solid state is used, the assumption of three double bonds in benzene is supported. The calculations of Fajans lead to the result that the linkage C-C in saturated hydrocarbons is nearly identical, from the point of view of energy, with the linkage of carbon atoms in the diamond; the energy absorbed in separating a gram atom of hydrogen single-linked to carbon is calculated as 11,700 cals. Fajans' calculations, however, have been criticised. General formulae for heats of combustion of various types of organic compounds are discussed, and the effects of substitution are considered. The coexistence of two substituents gives rise to an exaltation or depression of the heat of substitution of hydrogen by one of them: the carbonyl group reduces the heat of substitution of hydrogen by fluorine, whilst the hydroxyl group increases it, in aliphatic compounds. In aromatic compounds this effect is much more marked. There is some relation between the thermal effect of a substituent and its power of orientation.

The known results in many groups of organic compounds are discussed, and the difficulty of generalisation is apparent.

The book is well written and the results are precisely given; vague statements are avoided and the information cannot fail to be interesting to chemists as a whole.

J. R. Partington

Einführung in die mathematische Behandlung der Naturwissenschaften. *By W. Nernst and A. Schoenflies. Tenth enlarged and corrected edition. Munich and Berlin: R. Oldenbourg. Price: Bound, twelve gold marks; paper, ten gold marks.*

The textbook of Nernst and Schoenflies is well known to former students of Physical Chemistry. It gives a clear and neat account of the elements of the Differential and Integral Calculus, presented in a form suitable for direct application to physical and chemical problems and without obscuring the wood by the large trees of abstract theories on limits and series which, however necessary they may be to the mathematician, are merely repulsive and unnecessary in the eyes of the laboratory worker. There are some who argue that mathematics is best shunned by chemists altogether, as a discipline which can only blunt those fine instincts which in the past have led them through so much of the undergrowth which encumbers a new science. But much of this rank growth has since been cleared. The Phase Rule has laid swaths of possible compounds low, and much speculation is now debarred by a few simple principles. Whether a chemist would be better with or without mathematics, however, is a question which is best left to those who have no occasion to calculate and interpret the results of the laboratory, and the worker may be excused if he postpones his participation in the discussion and pushes on with the problems, which, in nearly all cases, require some mathematical knowledge for their solution. The fall of a stone cannot be represented without employing the ideas of the calculus, and it is hardly likely that the more complex problems of chemical reaction will prove any easier.

The additions made to the present edition are sections on the Heat Theorem by Nernst, and sections on Relativity and Crystal Lattices by Schoenflies. The former is very disappointing. It consists merely of a vague statement of the approximate equations, without any account of their application, and many difficult mathematical points which are involved in Nernst's own presentation in his other books are left untouched. The opportunity of clearing up some of these has been missed. The section on relativity will not have any bearing on chemical problems, and the theory of crystal lattices will also be of interest to a limited section of readers. The rest of the book is the same as in the older editions.

The printing is excellent but the paper is not of the best quality. The book can be recommended to students of physical chemistry, and to those beginning research work, as likely to be very useful to them. No space is wasted by irrelevant excursions into other fields; the powder is without jam, but then some of us object to being made to consume enormous quantities of jam to get a little valuable medicine.

J. R. Partington

Die Zustandsgleichung von Gasen und Flüssigkeiten. *By J. J. Van Laar. pp. X + 368. Leipzig: Leopold Voss, 1924.* There can be no doubt that van der Waals' characteristic equation for fluids represented a tremendous advance on anything that had previously been put forward. It gave an adequate qualitative description of the pressure-volume-temperature relations of fluids and at least an approximate representation of their quantitative behaviour. For example, it indicated a least volume (*b*) into which the fluid could be compressed; it also indicated a critical state. At the same time it was soon recognized that it could not be regarded as a final form. The two familiar factors *a* and *b* which enter into it could not both be independent of volume and temperature. Endless attempts have since been made to find how they must be made to vary in order that a successful representation of the facts shall be obtained. The present volume is one of the most thoroughgoing investigations into their variation based upon the large accumulation of experimental data made in the laboratory at Leiden and elsewhere.

The outcome of Dr. Van Laar's calculations is his conclusion that *a* depends upon volume but the variation is in many cases negligible. On the other hand *b* varies greatly with volume. The characteristic equation is finally written as $(p+a/v^2)\ (v-b_o)=RT\ (1+\frac{b_g-b_o}{v})$,

where $b_g/b_o=\frac{2\gamma a}{RT_cv_c}$ (γ=about 4/9)

and b_g is the limiting value of *b* when $v=\infty$.

Some dependence upon temperature must also be recognised. The equation is applied also to the question of vapour pressures and the author congratulates himself on how much can be learned without the quantum theory. The conclusions are supported by a mass of experimental data. Even those readers who may be tempted to differ from the author will certainly find the volume one of the best for exhibiting these data. Doubt as to the validity of his conclusions may arise when it is realised how flexible a formula can become when the number of constants in it is increased. The ideal gas equation with one constant, R, is obviously insufficient and may be discarded. Van der Waals' equation introducing three constants (R, a, b,) is much more successful. If it fits at large volumes the critical isotherm is wrong by something like 40% at the critical point. If a three constant formula is required then one based on Deterici's form would seem to be the best starting point: viz.

$$(p+a/T^{1/2}v^{5/3})(v-b)=RT,$$

for this automatically makes $v_c=4b$; $RT_c\ (P_cv_c)=3.75$ and $\left[\frac{T}{p}\frac{\partial p}{\partial T}\right]_{crit.}=7$ all of which are in close correspondence with experiments. It is known that this equation cannot fit even at large volumes but it seems to correspond with facts most nearly of any in the neighborhood of the critical point.

The general impression left is that the question is a very complicated one. This is said in no carping spirit. The wonder is, not that a complete equation fails to be found but that it is possible to achieve so great a success in representing by the use of so few constants the *average* properties of a congeries of molecules in random motion.

A. W. Porter

STUDIES OF SPARINGLY SOLUBLE SALTS, READILY OBTAINED FROM HOT SOLUTIONS OF REACTING SUBSTANCES. I

BY K. P. CHATTERJEE AND N. R. DHAR

When solutions of two ionised substances are mixed at the ordinary temperature and if there is the possibility of the formation of a sparingly soluble salt, in general immediate precipitation takes place. It is well known that the precipitate as it first comes out is rather of colloidal nature and is voluminous; this bulky precipitate gradually passes into the less soluble, compact, crystalline form. This behaviour is observable in most reactions of analytical chemistry; however, there are some exceptions. When we mix very dilute solutions of a phosphate and magnesia mixture (magnesium chloride, ammonium chloride and ammonia) a precipitate is not immediately obtained. It is well known that the precipitate of magnesium ammonium phosphate appears on vigorous shaking or rubbing the inside of the containing vessel with a glass rod. If the test-tube, having a very small quantity of the mixture containing magnesium ammonium phosphate, be heated carefully it might appear that more precipitation takes place; but if the tube be heated so that the solution boils vigorously, it will be found that practically the whole of the magnesium ammonium phosphate dissolves at the boiling temperature. Similarly, if solutions of sodium hydrogen tartrate and potassium nitrate are mixed together in dilute solutions, the precipitate of potassium hydrogen tartrate does not appear immediately. Ostwald explains this phenomenon by supersaturation. The potassium hydrogen tartrate that forms in the solution, remains at first in a supersaturated state, but after a time the solution passes through the metastable condition and becomes unstable and crystals of potassium hydrogen tartrate begin to appear. If the mixture of sodium hydrogen tartrate and potassium nitrate be carefully warmed, crystallisation of potassium hydrogen tartrate might take place; but if the heating be continued to boiling, practically the whole of the potassium hydrogen tartrate will dissolve. Similar behaviour is observable in the precipitation of ammonium hydrogen tartrate, potassium chloroplatinate, magnesium ammonium phosphate, magnesium ammonium arsenate etc. Unlike these cases there is a class of substances in which precipitation is hastened by heating the solution to boiling. The well known case of this type is that of calcium citrate. If a citrate and a calcium salt be mixed together and if the solutions are not very concentrated there is no immediate precipitation in the cold. Precipitation takes place immediately on heating the mixture, and even if the solution be boiled, no appreciable amount of the precipitate redissolves. It is also known that calcium hydroxide and a few more calcium salts come out as precipitates when their solutions are boiled. We have observed that this phenomenon of increased precipitation on heating the reacting solutions is of very common occurrence. Thus if a nickel salt and an oxalate or an oxalic acid solution be mixed, there is hardly any immediate precipitation. But if the mixture be heated, even to boiling, a copious precipitate of nickel oxalate is obtained. We have investigated many cases of this type. Thus, oxalates of copper, zinc, manganese, ferrous iron, magnesium, thorium, cobalt, etc, behave exactly in a similar way to the nickel salt. On the other hand, oxalates of calcium, strontium, barium, cadmium, thallium, silver, lead, etc., behave in a quite different way, especially the last two. Thus if dilute solutions of silver nitrate and an oxalate be mixed, a precipitate of silver oxalate is obtained almost immediately. If the tube be heated to boiling practically the whole of silver oxalate is dissolved. At first sight, the difference between these two types of substances may be ascribed to the difference of solubility of these substances at the different temperatures. It is a possible suggestion that calcium citrate, nickel oxalate, and copper oxalate, etc., are less soluble at a higher temperature than at a lower one, whilst the solubilities of the oxalates of silver, lead, thallium, cadmium barium, strontium, calcium, etc., in common with most normal salts increase with increase of temperature. We will discuss this point more fully later on. We have observed that the behaviour of strontium citrate is similar to that of calcium citrate, whilst the behaviour of the third analogue barium citrate is different from the other two.

This phenomenon is not restricted only to citrates and oxalates. Thus we have observed that tartrates of nickel, thorium zinc, manganese, cobalt, magnesium, etc., behave in the same way as the oxalates of these metals. In other words, these tartrates are more readily precipitated in the hot state from mixtures containing a soluble tartrate and the respective metallic salt. On the other hand, tartrates of copper, cerium and lanthanum, appear to be more soluble in hot water than in cold. Moreover benzoates of nickel, cobalt, chromium, zinc, etc., come out as precipitates more readily from hot solutions than from cold ones. Also, fluorides of copper, manganese, cobalt, nickel magnesium, etc., appear to be precipitated more quickly from hot solutions. Evidently this phenomenon of the rapid appearance of a precipitate from a hot solution is not restricted to a few calcium salts as has been hitherto supposed, but appears to us to be of common occurrence. The object of the present paper is to investigate this phenomenon thoroughly and if possible to suggest explanations of this peculiar behaviour in all cases. It is apparent that the same explanation will not be applicable to all cases, they being so very diverse. The following might be a possible explanation of this peculiar behaviour. As has already been said, increased precipitation with increase of temperature may take place if the solubility of the salt in question decreases with increase of temperature. In considering the above explanation of increased precipitation with increase of temperature it should be made certain that the salt is preserving the same composition throughout or whether any change in the amount of hydration is taking place with change of temperature. It can be assumed that the substance precipitated in the cold is more hydrated and more soluble than the salt precipitated at the boiling temperature. If these conditions occur, an explanation of the increased precipitation with increase of temperature is obtainable. Calcium citrate is a case in point and furnishes a very good instance of this type. We have observed and definitely proved that calcium citrate can exist as different hydrates containing different amounts of water. It has also been observed that the greater the degree of hydration, the greater the solubility. Thus, if a concentrated solution of sodium citrate and a concentrated solution of calcium chloride be mixed in the cold, a white gelatinous precipitate is immediately obtained. If the substance is rapidly separated from the mother liquor and pressed and dried, it is observed that the substance has the composition $Ca_3(C_6H_5O_7)_2\ 16H_2O$. This white substance is very easily soluble in water and is hygroscopic in the ordinary air. The solution of this substance decomposes at the ordinary temperature and readily gives a white precipitate of another hydrate of calcium citrate containing less amount of water of crystallisation. This white substance when purified and dried in air gives on analysis the formula $Ca_3(C_6H_5O_7)_2\ 6H_2O$. If hot solutions of sodium citrate and calcium chloride be mixed, still another hydrate having the composition $Ca_3(C_6H_5O_7)_2\ 4H_2O$ is formed. The first hydrate containing the maximum amount of water of crystallisation is very easily soluble in water, whilst the hydrate containing $6H_2O$ is sparingly soluble and the hydrate containing $4H_2O$ is the least soluble of the three and the solubility of the last hydrate decreases with increase of temperature. It appears to us that these facts go a long way in obtaining a complete explanation of the peculiar behaviour of citrates precipitated as calcium citrate in qualitative analysis. We have also investigated the case of strontium citrate and have got results similar to those of calcium citrate.

We have already observed that $Ca_3\ (C_6H_5O_7)_2\ 4H_2O$ which is obtained by mixing hot solutions of sodium citrate and calcium chloride is less soluble at the higher temperature than in the ordinary temperature. It is well known that calcium hydroxide and some other calcium salts behave in the same way. It may be argued that some of the substances which show increased precipitation with increase of temperature may behave in a similar way. In the case of calcium citrate as we have already said, the explanation of the increased precipitation at the higher temperature rests on the formation of different hydrates with different solubilities at different temperatures. But it may be assumed that in some cases the same hydrate will be formed when the solutions are mixed in the hot or in the cold. If it can be proved that the solubility of one and the same hydrate which does not change its composition when precipitated at different temperatures is less at a higher temperature than at the ordinary temperature then we can have an explanation of this phenomenon of the increased precipitation at high temperatures. If on the other hand the same hydrate obtainable in the hot or cold does not show a decreased solubility with increase of temperature we have to look to something else for an explanation of increase of precipitation with increase of temperature. As a matter of fact we have observed that the composition of several oxalates, tartrates, etc., remains consistently the same whether the salt is precipitated in the hot or cold. We have also observed that these salts do not show a decreased solubility with increase of temperature, but follow the normal behaviour of increased solubility with increase of temperature. We have tried to find an explanation for this class of substances in the phenomenon known as "velocity of precipitation". From chemical dynamics, we know that each chemical change has its own velocity or speed, and that rise of temperature markedly accelerates all chemical changes. The influence of temperature on a chemical change depends on the nature of the change itself, but it has been proved that the slower the change the greater is the influence of temperature[1]. Evidently, temperature should have some effect on the velocity of precipitation of substances. It also follows from our knowledge of chemical dynamics that instantaneous reactions as well as instantaneous precipitations are hardly affected by increase of temperature. In other words, it will be practically impossible to investigate the influence of temperature on a very rapid precipitation phenomenon such as the formation of silver oxalate or silver chloride. On the other hand temperature should have a marked effect on a slow precipitation process. Consequently, if we assume that the velocity of the appearance of nickel oxalate when dilute solutions of a nickel salt and an oxalate or oxalic acid be mixed, be not extremely great but has a measurable value, we are forced to the conclusion that the temperature will have some effect on this velocity and will accelerate the precipitation. In other words if we assume that the appearance of nickel oxalate takes a certain amount of time, then temperature will hasten the precipitation as it does accelerate all chemical changes. Evidently, the phenomenon of increased precipitation of substances like nickel oxalate, copper oxalate, etc., at higher temperatures can be explained on the basis of a measurable velocity of the appearance of the precipitate and the influence of temperature on it.

The experimental work in this paper will consist of: (1) determinations of the composition of the substances precipitated from the hot and the cold solutions; (2) determinations of the solubility of these substances at various temperatures; (3) determinations of the transition temperature of one hydrate into the other; and (4) investigation of the velocity of precipitation and the influence of temperature on it.

In order to find out whether salts prepared at the ordinary temperature differ in composition from those prepared in boiling condition, the reacting substances were mixed in one case at the ordinary temperature of the laboratory and in another case whilst they were boiling. The salts prepared in this way were freed from the mother liquor and unless otherwise stated, they were dried in air. Then they were analysed by suitable methods.

In order to determine the solubility at the ordinary temperature and at the higher temperature, a sufficient quantity of the salt is shaken with distilled water in a clean Jena glass flask. For the determination of the solubility at the ordinary temperature, the mixture is shaken until no more of the salt dissolves, and the liquid is then filtered, and about 200 cc of the filtrate is evaporated in a platinum dish. In most cases the residue was converted into sulphate with a little sulphuric acid and weighed as anhydrous sulphate. From the weight of the salt obtained, the amount of the original salt dissolved

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[1] Dhar: Ann. chim. (9) 11, 130 (1919).

per litre is calculated. For the determination of solubility at the boiling temperature, the mixture of salt and distilled water was boiled for a sufficient length of time for equilibrium to be attained. The liquid is then quickly filtered in a hot-water funnel and the temperature of the filtrate running down is noted. A measured volume is taken and evaporated and estimated as in the previous case.

Calcium Citrate

In the following pages, it will be shown that we have got four definite hydrates of calcium citrate. When approximately twice normal solutions of calcium chloride and sodium citrate are mixed, a precipitate similar to starch paste is obtained which is readily soluble in water. Addition of alcohol re-precipitates it from its aqueous solution. It is difficult to determine the composition of this salt as even at ordinary temperature it passes into another hydrate which is described later on and which is sparingly soluble.

In presence of an excess of alcohol, the velocity of transformation becomes much less, but as soon as the alcohol is filtered off, the salt readily passes into another hydrate. This unstable hydrate is very hygroscopic. Attempts have been made to analyse the unstable hydrate by carrying on the precipitation at 0°C and also by rapid centrifuging and quick washing and drying. The following figures will give an idea of the approximate composition of the salt. In the following analyses as well as in the other cases, a known weight of the substance is taken in a platinum crucible and heated strongly. A few drops of dilute sulphuric acid are added and the excess of acid evaporated and the residue is heated and weighed as sulphate.

In the following, only one result of analysis for each salt is given.

0.4386 gm. of the hydrate gives 0.2262 gm. $CaSO_4$ ∴ Ca = 15.1%

Calc. for $Ca_3(C_6H_5O_7)_2\ 16H_2O$, Ca = 15.2%

Hence the unstable and easily soluble hygroscopic calcium citrate has most probably the composition $Ca_3(C_6H_5O_7)_2\ 16H_2O$.

It has been already observed that the aqueous solution of the unstable hydrate gradually gives a precipitate of another hydrate. This hydrate which is much less soluble than the unstable hydrate can be readily obtained by mixing solutions of calcium chloride and sodium citrate at the ordinary temperature and setting the mixture aside for sometime. This is the hydrate which is generally obtained when a moderately concentrated solution of calcium salt and a citrate are mixed. The salt is filtered, washed, dried in the air at the ordinary temperature, and analysed.

0.3758 gm of the salt gave 0.2542 gm $CaSO_4$ ∴ Ca = 19.8%

Calc. for $Ca_3(C_6H_5O_7)_2\ 6H_2O$, Ca = 19.8%.

More than ten samples of the salt were made by mixing calcium chloride and sodium citrate of different concentrations at the ordinary temperature and in all cases, the hydrate obtained at the ordinary temperature has the composition $Ca_3(C_6H_5O_7)_2\ 6H_2O$. We could not confirm the existence of the hydrate $Ca_3(C_6H_5O_7)_2\ 7H_2O$, described in Beilstein's book.

This hydrate $Ca_3(C_6H_5O_7)_2\,6H_2O$ is fairly stable at the ordinary temperature, though it has a very slight tendency to pass into the lower hydrate which will now be described. If the hydrate $Ca_3(C_6H_5O_7)_2\,6H_2O$ be kept in the sun or if it is heated, it loses water and passes into the lower hydrate.

When boiling solutions of calcium chloride and sodium citrate are mixed, an immediate and abundant white precipitate is obtained, which is very sparingly soluble. This salt is freed from mother liquor, dried in air and analysed.

0.3074 gm salt gave 0.2192 gm $CaSO_4$. $\therefore$ Ca = 20.97%

Calc. for $Ca_3(C_6H_5O_7)_2\,4H_2O$, Ca = 21.05%

Hence the precipitate immediately obtained by mixing boiling solutions of calcium chloride and sodium citrate has the formula $Ca_3(C_6H_5O_7)_2\,4H_2O$.

If any of the above hydrates be heated in an air oven to 110° approximately, it gradually loses weight and after a time there is no further change in weight. This substance was analysed with the following results.

0.1156 gm salt gave 0.0932 gm $CaSO_4$. $\therefore$ Ca = 23.7%

Calc. for $Ca_3(C_6H_5O_7)_2\,\frac{1}{2}H_2O$, Ca = 23.6%.

This salt in contact with water rehydrates itself and forms $Ca_3(C_6H_5O_7)_2\,4H_2O$.

It has already been said that an aqueous solution of the unstable highest hydrate gradually gives the precipitate of $Ca_3(C_6H_5O_7)_2\,6H_2O$, in the cold. If however the solution be boiled, $Ca_3(C_6H_5O_7)_2\,4H_2O$ is copiously precipitated. We have also found out the limit of temperature below which only the hydrate $Ca_3(C_6H_5O_7)_2\,6H_2O$ is precipitated, by effecting the precipitation at different temperatures which were 32°, 40°, 50°, 60° 70°, 80°, 90°, 98°. Precipitation at temperatures up to 60°C produced the salt $Ca_3(C_6H_5O_7)_2\,6H_2O$, whereas at 70° and above the salt $Ca_3(C_6H_5O_7)_2\,4H_2O$ was produced.

The above results are interesting as they show the limit of temperature beyond which $Ca_3(C_6H_5O_7)_2\,6H_2O$ cannot be precipitated. In other words, in order to precipitate $Ca_3(C_6H_5O_7)_2\,6H_2O$ we should work at a temperature below 70°C. The results also explain why the hexahydrate decomposes when kept in the sun or slightly heated. This hexahydrate has a very small velocity of decomposition into water and the tetrahydrate when exposed. On keeping for a sufficiently long time in air at a temperature of about 30°C, for a month or so, the salt is found to be partially decomposed, as is seen from the following results.

0.0880 gm of the exposed salt gave 0.0614 gm $CaSO_4$ $\therefore$ Ca = 20.5%

Apparently the salt has decomposed into water and the tetrahydrate.

We have already said that the hydrate $Ca_3(C_6H_5O_7)_2\,\frac{1}{2}H_2O$ readily combines with water and forms the tetrahydrate. Consequently out of the four hydrates which we have obtained (viz, with 16, 6, 4 and ½ molecules of water) the tetrahydrate is the most stable.

We also tried to find out the velocity of precipitation of calcium citrate at different temperatures. With this object in view, solutions of calcium chloride and sodium citrate were mixed at different temperatures and the interval necessary for the appearance of a precipitate was noted. Here are some results. At the temperatures, 32° 40°, 50° 60°, 70° 80°, 90° and 98° the intervals respectively were 20 min, 15 min, 2 min, 1/2 min, and instantaneous in the last four cases. These results will be discussed later on.

Solubility of the citrates of calcium has been investigated. We have already observed that the unstable hydrate is extremely soluble. No quantitative measurement of the solubility of this hydrate could be made because of the extremely unstable nature of the substance.

The solubility of the hexahydrate and the tetrahydrate was determined in the manner indicated previously. The solubility of Ca_3 $(C_6H_5O_7)_2$ $1/2$ H_2O could not be obtained because on mixing with water this hydrate passes into the tetrahydrate.

Salt	Temperature	Grams per litre (of the salt)	Grams per litre (of the anhydrous salt)
$Ca_3(C_6H_5O_7)_2$ $6H_2O$	30°	2.45 gm	2.01 gm
	95°	2.76 gm	2.27 gm
$Ca_3(C_6H_5O_7)_2$ $4H_2O$	30°	2.51 gm	2.2 gm
	95°	2.1 gm	1.83 gm

At a glance it will be seen that the solubility of the hexahydrate increases with temperature, whilst the solubility of the tetrahydrate decreases with temperature.

When $Ca_3(C_6H_5O_7)_2$ $6H_2O$ is boiled with water for a sufficiently long time it passes into $Ca_3(C_6H_5O_7)_2$ $4H_2O$ as the following results will show.

0.3818 gm of the salt obtained from boiling the hexahydrate in contact with water for a sufficiently long time gave 0.2743 gm $CaSO_4$. ∴ Ca = 21.1%

Calc. for $Ca_3(C_6H_5O_7)_2$ $4H_2O$, Ca = 21.05%

As has been already said the tetrahydrate is the most stable of the hydrates. Exposure to sun or moderate heating does not decompose it. The tetrahydrate, when kept in water even for a long time, does not reform the hexahydrate. On the other hand the hexahydrate when kept in the sun for about 12 hours, is converted into the tetrahydrate. If the hexahydrate is heated in the water bath at 50°, it loses two molecules of water of crystallisation and passes into the tetrahydrate in eight hours. Decomposition of the hexahydrate was also investigated at 65°, 70° and 80° and is much quicker than at 50°C. At 65°C, exposure for an hour and a half is sufficient to decompose 0.3250 gm of the hexahydrate into the tetrahydrate.

The solubility curves of the hexahydrate and the tetrahydrate intersect at 52°C. In other words, this is the transition temperature of the two hydrates and at this temperature the two hydrates can be kept for an indefinite period in contact with water. This is remarkable, as this temperature is not far from that beyond which the hexahydrate is not precipitated as we have already shown, and when by mixing calcium chloride and sodium citrate we get the tetrahydrate.

From the foregoing results we get a satisfactory explanation of the peculiar behaviour observed on mixing a citrate and a calcium salt. In ordinary text books of organic chemistry, in explaining the reactions involved in the test of the citrate, the only suggestion thrown out is that calcium citrate is precipitated in the hot and not in the cold, because calcium citrate is less soluble at a higher temperature. We presume we have given a complete explanation of this peculiar behaviour. If a calcium salt and a citrate be mixed, there is the possibility of the formation of the readily soluble hydrate $Ca_3(C_6H_5O_7)_2$ $16H_2O$. But as has been proved, this hydrate is unstable and readily passes into the hexahydrate, which is generally obtained by mixing moderately concentrated solutions of the calcium salt and a neutral citrate in the cold. But if the solutions are dilute the hexahydrate is not usually precipitated in the cold, but on boiling, the sparingly soluble tetrahydrate is readily precipitated, because, like all chemical changes, temperature markedly accelerates the velocity of precipitation. In testing for a citrate by calcium salts, the precipitate which is obtained from a boiling solution is the sparingly soluble tetrahydrate $Ca_3\ (C_6H_5O_7)_2\ 4H_2O$. The above is the explanation of the peculiar behaviour in the test for a citrate by a calcium salt.

In the following citrates, oxalates and tartrates, only one result of analysis, as a rule, is given.

Strontium Citrate

The behaviour of strontium citrate is more or less allied to that of the calcium salt. When concentrated solutions of strontium chloride and sodium citrate are mixed, a precipitate of the nature of the unstable calcium citrate is obtained. This salt is very unstable and is readily soluble in water. This hydrate is too unstable to be partially purified and analysed and very quickly passes into the next hydrate of which the analysis is given below. This second hydrate is to be carefully dried in the shade. Exposure to tropical sunlight makes it lose its water of crystallisation until it attains the composition Sr_3 $(C_6H_5O_7)_2\ H_2O$.

0.6076 gm of the salt gave 0.4564 gm. $SrSO_4$. ˙. $Sr = 35.84\%$

Calc. for $Sr_3(C_6H_5O_7)_2\ 5H_2O$, $Sr = 35.95\%$

Hence it is evident that by mixing a cold solution of strontium salt and a neutral citrate, we get a white precipitate, which, when air dried at the ordinary temperature, has the formula $Sr_3(C_6H_5O_7)_2\ 5H_2O$.

This salt decomposes if it be placed in the sun. A certain specimen of the salt was exposed to the sun for a short time and analysed.

0.1620 gm of the salt gave 0.1234 gm $SrSO_4$. ˙. $Sr = 36.34\%$.

It is apparent that the salt has partly decomposed on exposure to tropical sunlight. Another sample was exposed to sunlight for a sufficient length of time until a constant weight was obtained and then it was analysed with the following results.

0.2770 gm of the salt gave 0.2300 gm. $SrSO_4$. ˙. $Sr = 39.61\%$

Calc. for $Sr_3(C_6H_5O_7)_2\ H_2O$, $Sr = 39.9\%$

$Sr_3(C_6H_5O_7)_2\ 5H_2O$ remains unchanged even if it be boiled with water. A certain sample of the salt, prepared in the cold, was boiled with water for some time and was dried in air and analysed.

0.2144 gm of the boiled salt gave 0.1624 gm $SrSO_4$. ˙. $Sr = 36.14\%$

Calc. for $Sr_3(C_6H_5O_7)_2\ 5H_2O$, Sr = 35.91%

If a solution of the unstable, readily soluble, strontium citrate be boiled, a copious precipitate is immediately obtained, which is apparently a mixture of $Sr_3(C_6H_6O_7)_2\ 5H_2O$ and $Sr_3(C_6H_5O_7)_2H_2O$ as the following results of analysis will show.

0.1070 gm of the salt thus precipitated gave 0.0848 gm $SrSO_4$ ∴ Sr = 37.86% $Sr_3(C_7H_6O_7)_2\ H_2O$ can be readily obtained by mixing boiling solutions of a strontium salt and a citrate. This salt is very stable. The pentahydrate when heated or exposed to tropical sunlight passes into this hydrate

When this monohydrate is kept in contact with water, the pentahydrate is not reformed.

0.2227 gm of the salt thus kept and then analysed gave

0.1847 gm of $SrSO_4$ ∴ Sr = 39.6%

Calc. for $Sr_3(C_6H_5O_7)_2\ H_2O$, Sr = 39.9%

Many samples of this monohydrate were obtained by mixing boiling solutions of a strontium salt and a citrate and analysed with the following results.

0.1294 gm of the salt gave 0.1080 gm. $SrSO_4$ ∴ Sr = 39.8%

Calc. for $Sr_3(C_6H_5O_7)_2\ H_2O$, Sr = 39.9%

Evidently it is clear that by mixing boiling solutions of a strontium salt and a neutral citrate, the white precipitate obtained has the formula $Sr_3(C_6H_5O_7)_2\ H_2O$.

An old sample of $Sr_3(C_6H_5O_7)_2\ H_2O$ was kept in an air oven at 110° for a number of days with no loss of weight. Consequently, at 110°, it is not possible to obtain a hydrate lower than the monohydrate. In this respect strontium citrate differs from calcium citrate. The solubilities of the two hydrates at different temperatures were determined in the same way as that of the calcium salt and the following results were obtained.

Salt	Temperature	Grams per litre (of the salt)	Grams per litre (of the anhydrous salt)
$Sr_3(C_6H_5O_7)_2\ 6H_2O$	30°	1.55	1.26
	95°	1.79	1.57
$Sr_3(C_6H_5O_7)_2\ H_2O$	30°	3.05	2.97
	95°	1.83	1.54

It is to be noted that the intersection of the solubility curves of the pentahydrate and the monohydrate is beyond 100°C as will be shown by producing the curves until they meet. The pentahydrate seems, therefore to be stable at 100°C in presence of water.

Nickel Oxalate

200 cc of seminormal nickel chloride and 250 cc of seminormal oxalic acid were mixed and kept at 29°C. An excess of oxalic acid was used to prevent the formation of a basic salt. After enough precipitate separated, it was collected, washed and dried. The analysis of the nickel oxalate was carried out in the following way.

(1). A weighed quantity of the salt was heated in a platinum crucible for some time and a drop of nitric acid was added and reheated and weighed as NiO. (2). A weighed quantity of the salt was dissolved in sulphuric acid and the solution was titrated with standard permanganate. (3). By means of combustion analysis, the amounts of water, carbon dioxide and nickelous oxide, left as residue, were directly determined and thus a complete analysis was made, from which the formula was calculated.

(1) 0.4950 gm of the salt gave 0.1890 gm NiO. ∴ Ni = 30%
Calc. for $3NiC_2O_4\,8H_2O$, Ni = 30.1%

(2) 0.3350 gm of the salt on titration with $KMnO_4$ showed 0.2674 gm of anhydrous salt ∴ Ni = 30.14% and H_2O = 24.6%
Calc. for $3NiC_2O_4\,8H_2O$, Ni = 30.1% and H_2O = 24.6%

(3) 0.1792 gm salt on combustion gave 0.0688 gm NiO, 0.0442 gm H_2O and 0.0806 gm CO_2, ∴ Ni = 30.2%, H_2O = 24.7% and CO_2 = 45%
Calc. for $3NiC_2O_4\,8H_2O$, Ni = 30.1% H_2O = 24.6% and CO_2 = 45.1%.

Consequently, by mixing solutions of a nickel salt and oxalic acid, at the ordinary temperature, the formula of the oxalate obtained is $3NiC_2O_4\,8H_2O$.

By mixing boiling solutions of nickel chloride and oxalic acid, a copious precipitate was immediately obtained. The salt was dried and analysed by the methods already indicated. Only one analysis is given below.

0.1482 gm of the salt gave on combustion 0.0592 gm NiO, 0.0330 gm of H_2O and 0.0684 gm CO_2. ∴ Ni = 31.4%, H_2O = 22.3%, CO_2 = 46.1%

Calc. for $3NiC_2O_4\ 7H_2O$, Ni = 31.1%, H_2O = 22.3% and CO_2 = 46.6%

Consequently, the formula of the salt obtained by mixing boiling solutions of nickel chloride and oxalic acid is $3Ni\ C_2O_4\ 7H_2O$, whilst the salt obtained at the ordinary temperature contains one molecule more of the water of crystallisation and has the formula $3NiC_2O_4\ 8H_2O$. The formula of the nickel oxalate given in Beilstein is $NiC_2O_4\ 2H_2O$. We could not verify this result.

Cobalt Oxalate

The salt was obtained at 30° and at the boiling temperature. The following are the analyses, one analysis in each case being given.

(1) 0.1046 gm of the salt precipitated at 30°, gave 0.0450 gm Co_3O_4, 0.0496 gm CO_2 and 0.0215 gm H_2O.
∴ Co = 31.6%, CO_2 = 47.4%
Calc. for $4CoC_2O_4\,9H_2O$, Co = 31.7%, CO_2 = 47%.

Consequently the hydrate obtained has the formula $4CoC_2O_4$, $9H_2O$

(2) 0.1112 gm of the salt precipitated from boiling solutions, gave 0.0490 gm of Co_3O_4, 0.05334 gm CO_2 and 0.0226 gm H_2O ∴ Co = 32.1%, CO_2 = 47.5% and H_2O = 20.1%.

Calc. for $CoC_2O_4 2H_2O$, Co = 32.2%, CO_2 = 48.1% and H_2O = 19.7%
Hence the salt precipitated at 100° has the formula $Co\ C_2O_4\ 2H_2O$.

In Beilstein, we find that the oxalate described has the formula $CoC_2O_4\ 2H_2O$. We have got this hydrate as well as another new hydrate of the formula $4\ Co\ C_2O_4\ 9H_2O$, which is obtainable by mixing oxalic acid and a cobalt salt in the cold and keeping the mixture for some hours.

Copper Oxalate

The following are the analyses, only one analysis in each case being given.

(1) 0.1368 gm of the salt precipitated at 30°C, gave on combustion, 0.0712 gm CuO, 0.0792 gm CO_2 and 0.0006 gm H_2O

$\therefore$ Cu = 41.6%, CO_2 = 58.7% and H_2O = 0.2%

Calc. for CuC_2O_4, Cu = 41.9%, CO_2 = 58.1% and H_2O nil.

Hence the formula of the salt precipitated at 30°C is CuC_2O_4.

(2) 0.1104 gm of the salt precipitated from boiling solutions, gave on combustion 0.0575 gm CuO, 0.0639 gm CO_2 and 0.0008 gm H_2O.

$\therefore$ Cu = 41.6%, CO_2 = 57.9% and H_2O = .7%

Calc. for CuC_2O_4, Cu = 41.9%, CO_2 = 58.1% and H_2O nil.

Hence, copper oxalate precipitated at 100°C has the formula CuC_2O_4. Beilstein describes two hydrates of the formula $CuC_2O_4\,H_2O$ and $CuC_2O_4\,1/2\,H_2O$. Both in the hot and the cold we got the anhydrous CuC_2O_4 precipitated.

Manganese Oxalate

(1) 0.2910 gm of the salt precipitated at 30°C, gave on titration with $KMnO_4$ 0.2323 gm of anhydrous oxalate and 0.0587 gm (by difference) of water. $\therefore$ Mn = 30.71% and H_2O = 20.1%

Calc. for $MnC_2O_4\,2H_2O$, Mn = 30.7% and 20.1%.

(2) 0.3683 gm of the salt precipitated from boiling solutions, gave on titration with $KMnO_4$ 0.2934 gm of the anhydrous oxalate. $\therefore$ Mn = 30.65%

Calc. for $MnC_2O_4\,2H_2O$, Mn = 30.7%

The solubility of this oxalate was determined at 36°C and 93°C. 200 cc of the clear filtrate obtained after saturation with the oxalate, were evaporated and the residue was strongly heated and weighed as Mn_3O_4.

	Temperature	Grams of anhydrous salt per litre
Salt precipitated in the cold	36°	·375
	93°	·780
Salt precipitated from boiling solutions	36°	·375
	93°	·789

Evidently the same hydrate is obtained at the ordinary and also at the boiling temperatures and the solubility of the salt increases with increase of temperature.

Beilstein has described two hydrates, namely containing 2.5 and 3 molecules of water of crystallisation, but we got only the hydrate containing $2H_2O$ both in the hot and in the cold.

Magnesium Oxalate

(1) Concentrated solutions of magnesium sulphate and oxalic acid were mixed and kept overnight at the ordinary temperature. A white crystalline precipitate was obtained. It was washed, dried, and analysed. Only one analysis is given below. 0.2576 gm of the salt precipitated at 30°C, gave 0.0608 gm MgO $\therefore$ Mg = 16.8%

Calc. for $MgC_2O_4\ 2H_2O$, Mg = 16.2%

Hence magnesium oxalate precipitated from concentrated solutions of magnesium sulphate and oxalic acid at 30°C has the formula $MgC_2O_4.\ 2H_2O$.

(2) When concentrated solutions of magnesium sulphate and oxalic acid are mixed in boiling conditions, a copious white precipitate is immediately obtained. The salt was washed, dried, and analysed, one analysis being given underneath. 0.2642 gm of the salt gave on titration with $KMnO_4$, 0.1944 gm of the anhydrous oxalate. ∴ Mg = 16.1%

Calc. for $MgC_2O_4\ 2H_2O$, Mg = 16.2%

Hence the formula of the salt precipitated at 100° is the same as that precipitated at 30°; it is $MgC_2O_4\ 2H_2O$

For solubility, 200 cc of the solutions were evaporated and the residues were treated with small quantities of sulphuric acid and heated until fuming ceased. These were weighed as $MgSO_4$ and calculations were made therefrom.

	Temperature	Grams of anhydrous salt per litre
Salt precipitated in the cold	36°	.338
	92°	.406
Salt precipitated from boiling solutions.	36°	.302
	92°	.393

Hence the same salt is precipitated both in cold and in hot. This salt also is more soluble at higher temperatures than at the ordinary temperature.

Kohlrausch[1] prepared supersaturated solutions of magnesium oxalate by neutralization of oxalic acid with magnesium hydrate and determined their molecular conductivities.

Ferrous Oxalate

(1) 0.1872 gm of the salt precipitated at 30°C gave 0.0824 gm of Fe_2O_3. ∴ Fe = 30.8%

Calc. for $FeC_2O_4\ 2H_2O$, Fe = 31.1%

When ferrous sulphate and oxalic acid are mixed, there is no immediate precipitation in the cold, but copious precipitation takes place when boiling solutions are mixed.

(2) 0.1756 gm of the salt precipitated from boiling solutions gave 0.0772 gm. Fe_2O_3. ∴ Fe = 30.8%.

Calc for $FeC_2O_4\ 2H_2O$, Fe = 31.1%

Evidently, the hydrate $FeC_2O_4\ 2H_2O$ is precipitated both in the hot and in cold.

Zinc Oxalate

(1) 0.7258 gm of the salt, precipitated at 30°C, gave on titration with potassium permanganate, 0.5840 gm of the anhydrous salt.

∴ Zn = 34.3%

Calc. for ZnC_2O_4, $2H_2O$, Zn = 34.6%

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[1] Sitzungsber. Akad. Wiss. Berlin, 1904, 1223.

When solutions of zinc salt and oxalic acid are mixed in the cold there is no immediate precipitate, but the precipitate of zinc oxalate comes out after a long time. On the other hand a copious white precipitate is obtained when boiling solutions of zinc salt and oxalic acid are mixed. The salt obtained at the boiling temperature was washed, dried and analysed with the following result.

(2) 0.9829 gm of the salt showed on titration with potassium permanganate 0.7900 gm. of anhydrous zinc oxalate. ∴ Zn = 34.2%

Calc. for Zn C_2O_4 $2H_2O$, Zn = 34.6%

Consequently the hydrate ZnC_2O_4, $2H_2O$ is precipitated both in the hot and in cold, when a zinc salt is added to oxalic acid.

Thorium Oxalate

(1) Thorium nitrate and oxalic acid were mixed and left for a long time at 30°. A white precipitate was obtained which was washed, dried and analysed.

0.1296 gm of the salt gave 0.0662 gm ThO_2 ∴ Th = 44.9%

Calc. for $Th(C_2O_4)_2$ $6H_2O$, Th = 45%

(2) When boiling solutions of thorium nitrate and oxalic acid are mixed, a copious white precipitate is obtained and the substance has a tendency to pass into colloidal state.

The salt was carefully washed and dried in air and analysed.

0.1774 gm of the salt gave 0.0905 gm Tho_2 ∴ Th = 44.8%

Calc. for $Th(C_2O_4)_2$ $6H_2O$, Th = 45%

Hence the formula of thorium oxalate precipitated both hot and cold, is $Th(C_2O_4)_2$ $6H_2O$.

Brauner[1] gives the composition of the air dried salt by the formula Th $(C_2O_4)_2$ $6H_2O$, obtained by mixing in the cold an oxalate and a thorium salt solution. We have obtained the same composition from boiling solutions as well. In Beilstein the hydrate described is Th $(C_2O_4)_2$ $2H_2O$ which is obtained on partial dehydration of the hexahydrate over sulphuric acid.

Magnesium Tartrate

(1) 0.4804 gm of the salt, precipitated at 30°, gave (on keeping in a hot air oven until a constant weight was obtained) 0.3836 gm anhydrous magnesium tartrate, from which 0.2670 gm anhydrous magnesium sulphate was got. ∴ Mg = 11.1% and H_2O = 20.7%

Calc. for Mg $(C_4H_4O_6)$, 2½ H_2O, Mg = 11.1% and H_2O = 20.7%

(2) When boiling solutions of magnesium sulphate and Rochelle salt were mixed, the precipitation was immediate.

0.6966 gm of this salt gave 0.3874 gm $MgSO_4$. ∴ Mg = 11.2%

Calc. for Mg $(C_4H_4O_6)$ 2½ H_2O, Mg = 11.1%.

(3) If any of the above salts be heated to 170°, until a constant weight is obtained, anhydrous magnesium tartrate, as proved by analysis, is obtained. This anhydrous salt, when moistened with water and dried on a water bath remains unchanged. For solubility, the following results were obtained.

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[1] J. Chem. Soc. 73, 984 (1898).

Salt	Temperature	Grams of the anhydrous salt per litre
Magnesium tartrate precipitated in the cold	30°	7.6
	90°	14.4
Magnesium tartrate precipitated in the hot	30°	7.5
	90°	14.5

It is evident the same salt is precipitated both in hot and cold. Beilstein gives $Mg(C_4H_4O_6)\ 4H_2O$, $Mg(C_4H_4O_6)\ 3H_2O$ and anhydrous magnesium tartrate. We could not verify the first two.

Manganese Tartrate

In the cold, this salt is slowly precipitated, but it comes out in a granular form. The amorphous salt is very quickly formed when boiling solutions are mixed.

(1) 0.5060 gm of the salt precipitated at 30°, gave 0.4334 gm anhydrous salt, which yielded 0.3260 gm manganous sulphate ∴ $Mn = 23.3\%$.

Calc. for $Mn(C_4H_4O_6)\ 2H_2O$, $Mn = 23.1\%$

(2) 1.0904 gm of the salt, obtained from boiling solutions, gave 0.6936 gm manganous sulphate. ∴ $Mn = 23.2\%$

Calc. for $Mn(C_4H_4O_6)\ 2H_2O$ $Mn = 23.1\%$

The anhydrous manganous tartrate is obtained by heating either of the above salts to 140°C. On moistening, this does not get hydrated again.

The same salt is precipitated both hot and cold. 1000 gm of the solution at 25°C contains 2.4 gm, and at 90°C 2.45 gm of anhydrous manganese tartrate.

Cobalt Tartrate

If concentrated solutions of cobalt sulphate and Rochelle salt be mixed, and if the mixture be kept undisturbed, a finely granular purple salt is gradually precipitated. If the mixture be stirred or if the solution be added hot, an amorphous pink salt is obtained. In this, as well as in the previous case, the precipitate is rather retarded if excess of the tartrate be added, owing probably to the formation of complex salts.

(1) 0.6956 gm. of the purple salt precipitated in the cold, gave on drying 0.5714 gm of anhydrous salt, which yielded 0.4290 gm of anhydrous cobalt sulphate. ∴ $Co = 23.4\%$ and $H_2O = 17.8\%$

Calc. for $Co(C_4H_4O_6)\ 2\frac{1}{2}H_2O$, $Co = 23.4\%$ and $H_2O = 17.6\%$

Dehydration of the above salt slowly takes place even at 60°C. On moistening and drying the anhydrous salt, it does not get hydrated again.

(2) 0.3570 gm of the pink salt precipitated from hot solutions gave on drying 0.2938 gm of the anhydrous salt which yielded 0.2148 gm anhydrous cobalt sulphate. ∴ $Co = 23.4\%$ and $H_2O = 17.7\%$

Calc. for $Co(C_4H_4O_6)\ 2\frac{1}{2}\ H_2O$, $Co = 23.4\%$ and $H_2O = 17.6\%$

The pink salts have composition and properties similar to those of the purple one. The only point of difference is the appearance and crystalline form.

1000 gm of the solutions of both purple and pink salts contain at 29°C 1.85 gm anhydrous cobalt tartrate, and at 84°C, 2.45 gm of the same.

The molecular volume of H_2O in these comes out to be 15.

Nickel Tartrate

It is not so easy to prepare this salt as the cobalt compound. In the cold, the precipitation is extremely slow and the salt is fairly soluble in water.

(1) 0.2486 gm. of the salt, precipitated at 30°C gave 0.1966 gm anhydrous tartrate $\therefore$ $H_2O = 20.9\%$

0.3240 gm of the original salt gave 0.0920 gm NiO, $\therefore$ $Ni = 22.3\%$

Calc. for $Ni\ (C_4H_4O_6)\ 3H_2O$, $Ni = 22.5\%$ and $H_2O = 20.7\%$

(2) 0.4608 gm of the salt, precipitated when boiling solutions of nickel chloride and Rochelle salt are mixed, gave 0.1368 gm NiO. $\therefore$ $Ni = 23.3\%$

Calc. for $Ni(C_4H_4O_6)\ 2\frac{1}{2}\ H_2O$, $Ni = 23.3\%$ (and $H_2O = 17.8\%$)

(3) Anhydrous nickel tartrate is prepared by heating at 170°C any of the above salts until the weight is constant. Moistening the anhydrous salt with water, gives a mixture containing $2\frac{1}{2}$ and 3 molecules of water of crystallisation, as the following shows. 0.1653 gm of the substance obtained by moistening the anhydrous salt and drying it in air, lost 0.0312 gm on keeping it at 170°C $\therefore$ Loss of water $= 18.8\%$

Calc. for $Ni(C_4H_4O_6)\ 2\frac{1}{2}\ H_2O$, $H_2O = 17.8\%$
and for $Ni(C_4H_4O_6)\ 3H_2O$, $H_2O = 20.7\%$.

Calcium Tartrate

When concentrated solutions are mixed at the ordinary temperature, a jelly-like precipitate is formed. This passes rapidly to a granular mass with evolution of heat, so much so that ether can be made to boil with this heat of transformation.

(1) 0.2402 gm of the salt precipitated in the cold, gave 0.1246 gm $CaSO_4$ $\therefore$ $Ca = 15.3\%$

Calc. for $Ca\ (C_4H_4O_6)\ 4H_2O$, $Ca = 15.4\%$.

(2) 0.4950 gm of the salt precipitated in the hot, gave 0.2596 gm $CaSO_4$. $\therefore$ $Ca = 15.45\%$

Calc. for $Ca(C_4H_4O_6)\ 4H_2O$, $Ca = 15.4\%$

(3) 1.0650 gm of the salt went on losing weight, when kept at a temperature of 170°. The loss was slow. After 5 hours heating the loss was found to be about 12%; after 15 hours heating it came to about 24%. Finally, it stood constant at 25.6%

Calc. for $Ca(C_4H_4O_6)\ 4H_2O$, $Ca = 15.4\%$ and $H_2O = 27.6\%$

Calc. for $Ca(C_4H_4O_6)\ 3\frac{1}{2}\ H_2O$, $Ca = 15.9\%$ and $H_2O = 25.1\%$

Evidently this new salt is $4\ Ca(C_4H_4O_6)\ H_2O$, as later experiments show.

(4) This partially anhydrous salt gets hydrated when moistened with water and dried in air. The gain is 25.4%.

Calculated for $Ca(C_4H_4O_6)\ 1/4\ H_2O$ passing into $Ca(C_4H_4O_6)\ 3H_2O$ the gain is 25.1%

0.2522 gm of the supposed Ca $(C_4H_4O_6)$, $3H_2O$ gave 0.1406 gm $CaSO_4$ ∴ Ca = 16.4%

Calc. for $Ca(C_4H_4O_6)\ 3H_2O$, Ca = 16.5%

In Beilstein, we find only the tetrahydrate. Consequently a new hydrate $Ca(C_4H_4O_6)\ 3H_2O$ is formed on hydration of $4Ca(C_4H_4O_6)\ H_2O$.

Strontium Tartrate

These salts are prepared in the same way as the calcium salts

(1) 0.6818 gm of the salt precipitated at 30°C, lost 0.1610 gm on strong heating ∴ H_2O = 23.6%

0.7412 gm of the salt gave 0.4452 gm $SrSO_4$ ∴ Sr = 28.7%

Calc. for $Sr(C_4H_4O_6)\ 4H_2O$, Sr = 28.9% and H_2O = 23.6%

(2) 1.0936 gm of the salt precipitated from boiling solutions lost 0.0402 gm. on heating to 170° ∴ H_2O = 3.7%

0.4368 gm of the salt gave 0.3150 gm $SrSO_4$ ∴ Sr = 34.2%

Calc. for $Sr(C_4H_4O_6)\ H_2O$, Sr = 34.5% and H_2O = 7.09%

and $Sr(C_4H_4O_6)\ 1/2\ H_2O$, Sr = 35.8% and H_2O = 3.6%

It appears that the salt precipitated from the boiling solutions and dried in air has the formula $Sr(C_4H_4O_6)\ H_2O$ and this monohydrate, on heating to 170°C does not lose the whole of its water and most probably becomes converted into the hemihydrate $Sr(C_4H_4O_6)\ 1/2\ H_2O$.

Ferrous Tartrate

It is very difficult to prepare this salt in the cold. Being very soluble, it could not be thoroughly purified.

(1) 0.2486 gm of the salt precipitated at the ordinary temperature, lost nothing when heated to 170°C. H_2O is nil.

The above salt gave 0.0926 gm Fe_2O_3 ∴ Fe = 26.1%

Calc. for $Fe(C_4H_4O_6)$, Fe = 27.4% and water is nil.

(2) 0.7134 gm of the salt, precipitated when boiling solutions are mixed, lost nothing when heated to 170°C and yielded 0.2646 gm Fe_2O_3. ∴ Fe = 25.9%

Calc. for $Fe(C_4H_4O_6)$, Fe = 27.4% and water is nil.

It has already been observed that the salts could not be purified. It seems the same salt $Fe(C_4H_4O_6)$ is obtained in the hot and in the cold.

The Velocity of Precipitation and the Influence of the Temperature on it.

From the foregoing pages, it will be seen that in most cases the same hydrate is precipitated in the hot and in the cold. Also it will be seen that in almost all cases the solubility of these hydrates increases with increase of temperature. Consequently it is impossible to find out an explanation of the rapid increase of precipitation when a cold mixture of an oxalate solution and a metallic salt solution, say of magnesium, be heated. We have already observed that when a concentrated solution of magnesium sulphate and oxalic acid be mixed at the ordinary temperature, no precipitate is immediately obtained. But if the mixture be heated, a copious precipitate of magnesium oxalate is obtained.

We have also proved that the hydrate obtained in the hot and the cold has the same formula, namely $MgC_2O_4\,2H_2O$, and that the solubility of this hydrate increases with increase of temperature. In order to explain the peculiar behaviour of increased precipitation, on heating the reacting solutions, we have to look for its explanation in the phenomena of the velocity of precipitation of these substances. We have attempted to measure this velocity of precipitation by adopting different methods. Method (1) is, mixing the reacting substances at a definite temperature and taking out from time to time a measured volume of the unacted substance with the help of a pipette, to the nozzle of which was attached a rubber tubing, stuffed with cotton wool. Seminormal manganous sulphate of known strength was mixed with potassium oxalate of equivalent strength and left at a constant temperature. From time to time, a measured volume of the unchanged substance was taken out with the help of a pipette and the unchanged oxalate was estimated by titrating against permanganate. The following results were obtained.

At 30° Time	cc N/10 $KMnO_4$ for 10 cc solution		K_0 (Zero molecular)
0 minutes	72.8		
2	45.7		.1022
4 ”	21.55		1320
6 ”	15.65		.1120
8 ”	10.9		.1031
		mean	.1123

The solutions were diluted and mixed and in most cases the same velocity coefficient was obtained at the same temperature.

It was very soon realised that it was very different to reproduce these results. Very slight shaking affects the results to a great extent. In order to find out the temperature coefficient of this velocity of precipitation, measurements were also made at 4°C by mixing 50 cc seminormal potassium oxalate and 50 cc seminormal manganous sulphate both kept at 4°C. The following results were obtained.

At 4°C	Time in minutes	$KMnO_4$ for 10cc solution (168.8cc $KMnO_4$ = 10cc oxalate)		K_0
	2	70.5		.039
	4	56.9		.042
	6	47		.042
	10	42		.030
	12	33.3		.033
	14	24.6		.038
	16	16.04		.045
	18	40		.051
			mean	.04

Applying the Arrhenius formula, $\log_e \frac{K_1}{K_2} = \frac{A(T_1 - T_2)}{T_1 \times T_2}$, we get $A = 1447$ and $\frac{Kt+10}{Kt} = 1.52$

Attempts were made to find out the velocity coefficient whilst the reacting mixtures were being continually shaken. But no definite conclusion with regard to the order of the velocity of precipitation could be arrived at. In order to avoid supersaturation, a little manganous oxalate was added at the beginning of the experiment but this did not help in getting concordant results calculated as zero, uni- or bimolecular formula. It was also observed that by mixing seminormal manganous sulphate and an equivalent quantity of potassium oxalate, the appearance of visible precipitation takes place in 40 seconds at 30°C, whilst at 0° it takes 2 minutes, which gives Arrhenius $A = 1315$ and $\frac{Kt+10}{Kt} = 1.48$.

A similar experiment made with zinc sulphate and potassium oxalate gives the interval for visible appearance of precipitation as 1 minute and 51 seconds at 29°C and 5 minutes 30 seconds at 0° which would give $\frac{Kt+10}{Kt} = 1.5$ (nearly).

Method (2). The mixture of zinc sulphate and potassium oxalate was kept in a beaker over a piece of paper ruled with black lines, and the time was noted when the black lines just disappeared, due to the turbidity of the mixture from precipitation of the solid oxalate. In this case the solution was kept constantly stirred. At 29°C the disappearance of the black lines took place in 136 seconds whilst at 3° it took 660 seconds. These results give the Arrhenius constant $A = 2204$ and $\frac{Kt+10}{Kt} = 1.90$ In the former cases, the reacting mixture was not stirred at all, while in the latter case it was continually shaken. It seems therefore that the temperature accelerates the velocity of precipitation to a greater extent when the reacting substances are shaken than when the velocity is determined without shaking the mixture. It is of interest to note that Marc[1] showed that the velocity of crystallisation of supersaturated solutions of substances like potassium sulphate follows the bimolecular formula, whilst we have got agreement according to zero molecular formula[2].

The value of the temperature coefficient for 10° rise obtained by Marc is 1.6 whilst our value is 1.5. Moreover Jablczynski[3] obtains the value 2 for the temperature coefficient of the velocity of formation of silver bromide and silver chloride.

Method (3) We also attempted to obtain the velocity of precipitation from measurements of conductivities. We mixed solutions of a salt (e.g. manganous sulphate or zinc sulphate) and an oxalate and measured the resistance of the mixture. At the very outset we were surprised to find that the resistance changes very slightly though an appreciable amount of the oxalate

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[1] Z. physik. Chem. **61**, 385 (1908).
[2] Compare Dhar: Z. anorg. Chem. **121**, 156 (1922); J. Chem. Soc. **111**, 727 (1917).
[3] Z. physik. Chem. **82**, 115 (1913).

crystallised out. In order to find out an explanation, we had to make some preliminary experiments. We mixed 50 cc of N/50 NaCl and N/50 $AgNO_3$. We determined the resistance 45 seconds after the mixing. The value of this resistance did not change with time. It appears, therefore, that the precipitation has probably been finished within this 45 seconds. If we mix together, say, potassium oxalate and manganous sulphate we get manganous oxalate and potassium sulphate. As most of the manganese oxalate goes out as precipitate, the conductivity of the mixture should decrease appreciably. But as a matter of fact, in most cases we got a slight decrease of conductivity. We thought that the explanation might have something to do with the phenomenon of supersaturation. Incidentally we studied the molecular conductivity of supersaturated solutions of sodium acetate, calcium chloride, etc. In the case of sodium acetate and in the case of calcium chloride we found that in concentrated solutions, the curve of molecular conductivity with dilution shows definite breaks. In other words, at certain concentration instead of increasing with dilution, the molecular conductivity slightly decreases with dilution. In a foregoing paper, it has been observed that breaks of that nature which are so common in nonaqueous solutions are expected even in aqueous solutions of electrolytes, if determination could be made with sufficiently concentrated solutions.[1]

Summary

(1) Citrates of calcium and stronium, oxalates and tartrates of copper, zinc, magnesium, manganese, cobalt, nickel, iron (ferrous) and thorium, are precipitated more readily from boiling solutions of a citrate or an oxalate or a tartrate and a salt solution of the respective metal than when the reacting substances are mixed in the cold. The phenomenon of increased precipitation on heating the solutions of the reacting substances is of common occurrence.
(2) The following salts have been prepared and described:—

(a) $Ca_3(C_6H_5O_7)_2\ 16H_2O$; $Ca_3(C_6H_5O_7)_2\ 6H_2O$; $Ca_3(C_6H_5O_7)_2\ 4H_2O$ and $Ca_3(C_6H_5O_7)_2\ 1/2\ H_2O$.
(b) $Sr_3(C_6H_5O_7)_2\ 5H_2O$; $Sr_3(C_6H_5O_7)_2\ H_2O$.
(c) $3NiC_2O_4\ 8H_2O$; $3NiC_2O_4\ 7H_2O$
(d) $4CoC_2O_4\ 9H_2O$; $CoC_2O_4\ 2H_2O$
(e) CuC_2O_4
(f) $MnC_2O_4\ 2H_2O$
(g) $MgC_2O_4\ 2H_2O$
(h) $FeC_2O_4\ 2H_2O$
(i) $ZnC_2O_4\ 2H_2O$;
(j) $Th(C_2O_4)_2\ 6H_2O$
(k) $Mg(C_4H_4O_6)\ 2\frac{1}{2}\ H_2O$; $Mg(C_4H_4O_6)$
(l) $Mn(C_4H_4O_6)\ 2H_2O$; $Mn(C_4H_4O_6)$
(m) $Co(C_4H_4O_6)\ 2\frac{1}{2}\ H_2O$; $Co(C_4H_4O_6)$
(n) $Ni(C_4H_4O_6)\ 3H_2O$; $Ni(C_4H_4O_6)\ 2\frac{1}{2}\ H_2O$; $Ni(C_4H_4O_6)$

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[1] Compare Dhar: Z. Elektrochem. 20, 60 (1914).

(o) $Ca(C_4H_4O_6)\ 4H_2O$; $4Ca(C_4H_4O_6)\ H_2O$; $Ca(C_4H_4O_6)\ 3H_2O$.
(p) $Sr(C_4H_4O_6)\ 4H_2O$; $Sr(C_4H_4O_6)\ H_2O$; $Sr(C_4H_4O_6)\ 1/2\ H_2O$
(q) $Fe(C_4H_4O_6)$

(3) Molecular volume of water of crystallisation in some of these sparingly soluble salts, has the value 15 or 16,—practically the same as obtained with the readily soluble salts containing water of crystallisation.

(4) The velocity of precipitation of some oxalates and the influence of temperature on it have been investigated. It is observed that when the reacting mixture is not agitated, the velocity of the reaction apparently follows the zero-molecular formula $(K_0 = \frac{}{t})$ and $\frac{Kt+10}{Kt} = 1.5$

(5) Incidentally it has been observed that the molecular conductivities of very concentrated solutions of calcium chloride, sodium acetate etc. do not go on increasing with dilution, but at certain concentrations slightly fall off.

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Allahabad, India.
April 16, 1924.

ON THE STABILITY OF COLLOIDAL SOLUTIONS
PART I. ALUMINIUM HYDROXIDE SUSPENSION

BY K. C. SEN

In a recent paper it was observed that an undialysed sol of ferric hydroxide required more of an electrolyte for coagulation than a dialysed sol, and the following results were obtained. The concentration of the sol, that is, the iron content was the same in both cases, while the chlorine content was obviously different.

Electrolyte	cc. of electrolyte required for coagulating 5 cc. of	
	dialysed sol	undialysed sol
KNO_3 2N	3.0	6.1
$BaCl_2$ 2N	3.2	7.2
Mg SO_4 N/200	0.8	1.6
Cd SO_4 N/200	0.6	1.8

It was remarked in that paper that one possible explanation of this behaviour may be that small quantities of hydrochloric acid might have a peptising influence over ferric hydroxide, the removal of which by dialysis makes the sol less stable. Similar instances are also known in the case of arsenious sulphide where addition of H_2S makes the sol more stable towards monovalent positive ions. It is well known that many colloids owe their stability to the presence of adsorbed electrolytes. Thus colloidal manganese dioxide[1] coagulates on dialysis. The investigations of Ruer[2], and Hantzsch and Desch[3] show that well dialysed colloidal ferric hydroxide still contains some chloride. In fact it may be taken for granted that in all experiments on colloid precipitation, the colloids were never free from peptising electrolytes, the quantity of which has varied between wide limits in the samples of different investigators working on the same colloid.

In 1917, Neidle[4] showed in an interesting paper, that the stability of ferric hydroxide hydrosol was dependent not so much on the method of preparation as has so long been assumed, but to a greater extent on the purity and concentration of the sols employed. He prepared a number of perfectly clear hydrous oxide sols. In each series the iron concentration was constant, while the chlorine content was varied by the addition of known amounts of hydrochloric acid. The sols were precipitated by potassium sulphate solution, and

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[1] Ganguly and Dhar: J. Phys. Chem. 26, 703 (1922).

[2] Ruer: Z. anorg. Chem. 43, 85 (1905).

[3] Hantzsch and Desch: Ann. 323, 28 (1902); compare also, Duclaux: J. chim. phys. 5, 29 (1907).

[4] Neidle: J. Am. Chem. Soc. 39, 2334 (1917).

the amount of salt required for the complete precipitation of the sol was taken as a measure of its relative stability.

The data showed that for a given iron concentration the stability increases with the chlorine content, while for sols of a given purity, i.e. ratio equivalents Fe: equivalents Cl, the stability decreases as the concentration increases, this being most pronounced for very pure sols.

In recent years the stability of colloidal solutions has been much examined and it has been shown that in all precipitation experiments, the influence of the concentration of the colloidal solution must be taken account of. No such attention has however been paid to another important cause affecting the stability of suspensoids, namely the amount of stabilising agent present in the system. Unless the amount of the stabilising agent is known and experiments are carried out at the same concentrations of the stabilising agents, it is obvious that the results obtained in the coagulation experiments of two sols of the same substance will be different. In other words, the stability of a sol is dependent not only on its concentration, but also on the amount of impurity it contains.

In considering the coagulation of ferric hydroxide sol, it is evident from the results of Neidle, that the stability increases with the increase in the amount of HCl added to a certain extent and then decreases. At the higher concentration of the acid, a portion of the colloid is dissolved with the formation of ferric salt. It is interesting and theoretically important to enquire the cause of this increasing stability on the addition of slight quantities of hydrochloric acid. Neidle considers that, by the addition of slight amounts of acid, more stable oxychlorides are formed. According to him therefore we have to assume a series of oxychlorides of varying composition with the progressive addition of hydrochloric acid. It will be shown later on that the phenomenon can be explained equally well on the assumption that greater quantities of hydrogen ion are adsorbed by the ferric hydroxide and this increases the stability of the colloid.

It is apparent from what has been already stated that in order to study completely the stability relations of a colloid, a systematic attempt should be made to study the coagulation of different colloids with varying degree of electrolyte content. In order to obtain some experimental results of this nature, some experiments were designed similar to that made by Neidle, by adding varying quantities of stabilising electrolyte to well dialysed sol and then determining the precipitation value of a fixed electrolyte with this sol. A difficulty was however soon experienced—namely an uncertainty as to whether true equilibrium occurs between the dialysed colloid and the added electrolyte. Unless an equilibrium is reached between the colloid and the electrolyte, whereby with increasing concentration of the electrolyte more of it is adsorbed by the colloid particles, the exact role of the stabilising agent is difficult to explain. For, it is generally assumed that only that portion which is adsorbed can be effective in the stabilisation of the sol. It is therefore important to investigate first whether any stable equilibrium point is reached or not. Another point of importance is that though dialysis is theoretically a reversible phenomenon, in actual practice often it is not so. Thus the last traces of chloride cannot be easily dialysed out from a ferric hydroxide sol. Hence we cannot start with a sol of zero impurity. In our experiments with ferric hydroxide, we have found that it is very difficult to obtain an equilibrium point with hydrochloric acid.

Considering all these facts it occurred to me that before beginning to work on a colloid prepared before hand, it would be better to obtain some comparative data on some substance which can be obtained in a pure state, and which can be easily peptised by means of a suitable peptising agent. In a previous paper[1] I have studied the peptisation of hydroxides by different acids, and these hydroxides seemed to be suitable to start with in this investigation. It has been observed that freshly precipitated and well washed aluminium hydroxide can be peptised very readily by means of benzoic, acetic, propionic, hydrochloric acids, etc. When very small quantities of acids are used, the suspensions of the hydroxide are turbid, pass through filter papers, and are stable for at least 48 hours. With weak acids like acetic, benzoic, and propionic acids, the equilibrium point is reached quite readily; but with hydrochloric acid, the acid is continually adsorbed for some time by the hydroxide, and the conductance of the mixture hydroxide $+HCl$ falls gradually with time. For this reason, hydrochloric acid has not been used in peptising the hydroxide, and in general 24 hours have been allowed for the equilibrium to set in.

The stability of the suspension was measured against a standard potassium sulphate solution by coagulating a known volume of the suspension. Both the amount of the peptising acid as well as that of the concentration of the suspension have been varied. The determination of the exact coagulation point has been a matter of considerable difficulty, for the amount of electrolyte necessary to coagulate completely the suspension varied so much with the time employed, that no satisfactory data could be obtained. Hence it was decided to take that concentration of the electrolyte which coagulated the suspension immediately as the precipitating concentration of the electrolyte. By this method reproducible values were obtained, but the results were only relative and an appreciable error was introduced to which attention will be called later on.

The following results were obtained:—

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[1] Sen and Dhar: Kolloid-Z. 33, 193 (1923).

(a) Stabilising Agent—Benzoic Acid

Conc. of the acid in millimoles per litre	Purity of the suspension—ratio $\frac{\text{millimole } Al_2O_3}{\text{millimole acid}}$	ccs. of N/1000 K_2SO_4 req'd to coagulate 5cc. of the original suspension (6.43 millimole Al_2O_3 per litre)	suspension 1/2 diluted (3.215 millimole Al_2O_3 per litre)	suspension 1/4 diluted (1.6075 millimole Al_2O_3 per litre)
0.312	20.6	2.5	2.4	2.1
0.624	10.3	4.5	4.1	3.9
0.78	8.24	5.0	4.4	4.0
0.936	6.86	5.5	5.0	4.55
1.092	5.88	6.0	5.3	4.6
1.248	5.15	6.5	5.4	4.6
1.404	4.58	6.5	5.5	4.65
	(b) Stabilising Agent—Acetic Acid			
3.08	2.087	3.0	2.6	2.3
6.16	1.043	3.5	2.9	2.75
9.14	0.696	4.0	3.3	3.0
12.32	0.521	4.6	3.8	3.7
15.4	0.417	5.1	4.4	4.2
18.48	0.348	5.6	5.0	4.9
	(c) Stabilising Agent—Propionic Acid.			
2.4	2.68	2.3	2.15	1.9
4.8	1.34	2.7	2.6	2.5
7.2	0.893	3.7	3.6	3.4
9.6	0.67	4.5	4.35	4.2
12.0	0.446	5.5	5.35	5.1
14.4	0.383	6.5	6.3	6.1

From the above results it will be observed that with the same concentration of the suspension and increasing quantities of the stabilising agents, the suspension becomes more stable towards potassium sulphate. Also, with suspensions having the ratio Al_2O_3/acid equal, the stability decreases with the decrease in the concentration of the suspension. These results are very interesting from the fact, that the stability of a suspension or homogeneous colloidal solutions is dependent on the concentration as well as on the amount of the peptising agent contained in the system. A well dialysed sol is consequently less stable than an undialysed one and the anomalous results recorded by several investigators[1] on the coagulation of sulphide sols when sulphuretted hydrogen is present may be explained on the basis of these experiments.

An examination of the results further show that though the concentration of benzoic acid is less than that of acetic or propionic acid, it acts as a better

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[1] Mukherjee and Sen: J. Chem. Soc. 115, 461 (1919); Lottermoser: J. prakt Chem. (2) 75, 293 (1907).

stabilising agent. This is in accord with the fact as has been observed by me that benzoic acid is much more adsorbed than either acetic or propionic acid. Propionic acid is itself slightly more adsorbed than acetic acid and this explains the fact that at equal concentrations propionic acid is a better stabilising agent than acetic acid. It is apparent therefore that adsorption is playing an important rôle here.

It will be further observed that the curve, Fig. 1, obtained by plotting the acid concentration against the amount of electrolyte necessary for coagulation shows a well defined curvature in the case of benzoic acid. In the case of propionic acid the curve, Fig. 2, is a straight line and on being produced backwards, cuts the ordinate at a point well over zero. Similar is also the case with acetic acid. Since however at the zero concentration of the acid the stability is necessarily zero, the curve should pass through the zero point. Neidle has also obtained similar results, but he considers that the colloid may be stable even at the negative side of the abscissa, but he does not discuss this "negative stability" of colloidal solutions. It appears to me that this fact is due to experimental error involved in the determination of the coagulation point of colloids and incidentally my results show the amount of error that is possible in these experiments. The dotted curve has been drawn parallel to the experimental curve and probably the theoretically correct values may be obtained from it.

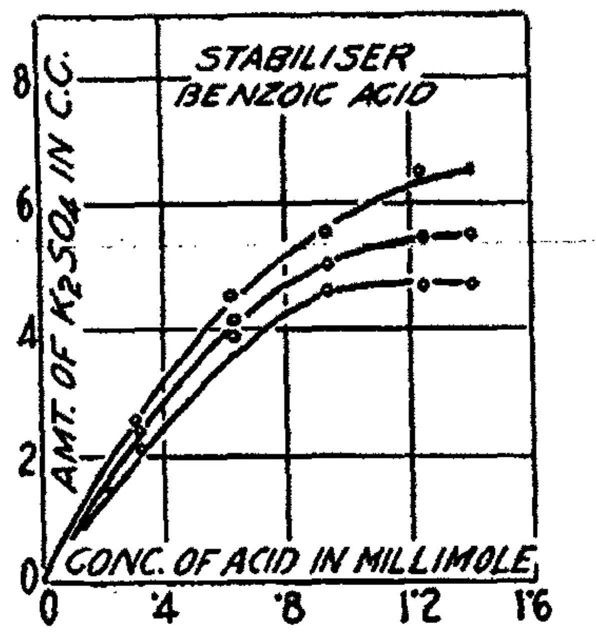

Fig. 1

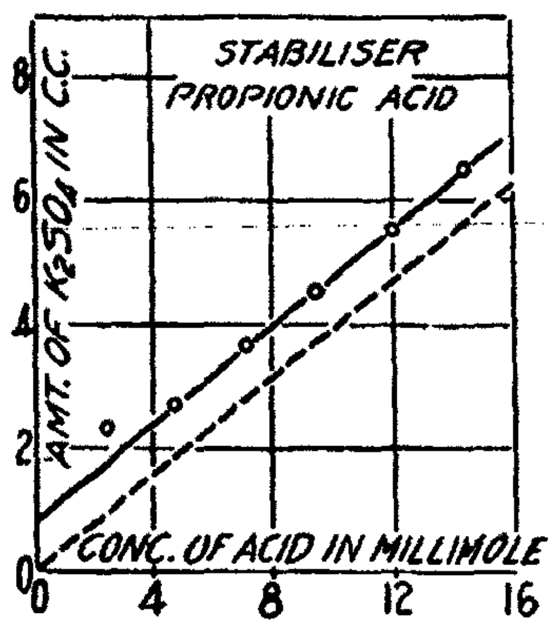

Fig. 2

Another interesting fact that may be discussed here is what happens if the concentration of the acid is increased more and more. Will the colloid or suspension be stabilised more and more *ad infinitum?* With an increase in the amount of acid, say in the case of aluminium hydroxide suspension, two things may happen. Firstly, since the suspension in this case is positively charged, the increasing concentration of the negative ion of the acid will have a coagulating effect on it, and secondly some of the hydroxide may be actually dissolved in the acid forming a salt. It has also been found by me that in the case of these acids the amount of adsorption reaches a maximum with increase in the concentration of the acid. The curve with benzoic acid shows that the stability of the suspension with the addition of the acid reaches a maximum. Neidle also observed that with increasing concentration of HCl, the stability of a ferric hydroxide colloid reaches a maximum and then decreases. He found also that with higher amounts of HCl, a little quantity of the colloid dissolved in the acid forming salt which could be tested after coagulation of the colloid. In my investigation, no salt formation was observed because the acid concentration was usually small. Theoretically however a point of maximum stability should occur with increasing concentration of the stabilising acid.

It is of interest here to discuss the constitution of hydroxide colloids. There is a prevalent view that the colloidal hydroxides are something like oxychlorides with a variable composition and Pauli and Matula[1] have proposed even a definite formula for the ferric hydroxide colloid. I have however repeatedly observed that if the concentration of the acid be small, and specially if the acid be weak like acetic acid, ferric hydroxide adsorbs the acid appreciably without any formation of a salt, and the adsorption is reversible. Since the colloids are positively charged and since no salt formation can be traced, it is better to assume that the H^+ ion is preferentially adsorbed which stabilises the colloid or suspension. It has been found that this adsorption of the hydrogen ion increases with the increase in concentration of the acid and reaches a maximum, and hence this adsorption view can explain the greater stability of the colloids with the increase in the amount of the stabilising agent without assuming the formation of any stable oxy-salts. The amount of adsorption will depend both on the amount of the colloidal substance as also on the amount of the acid present, and hence no simple relation exists between the two. Hence the composition of the colloid will vary between wide limits. It is an well known fact that when the concentration of the adsorbable solute is low, the adsorption is practically complete. This is known in the case of charcoal and iodine and has been found by me to be the case also with acids and hydrated oxides. The great difficulty of removing the last traces of HCl from ferric hydroxide sol by dialysis, a fact which has been supposed to agree very well with the assumption that a definite oxychloride exists, probably hinges on the same phenomenon as that in which we find that in small concentrations of an adsorbable solute practically the whole of it is adsorbed by a substance say hydrated ferric oxide.

From my experimental results, it will be observed that with aluminium hydroxide suspension, the greater the concentration of the suspension, the greater is its stability towards electrolytes. These results are in agreement with the law enunciated in a foregoing paper that the greater the concentration of the sol, the greater the stability towards electrolytes, the purity of the sol remaining the same.

Summary

(1) In investigating the stability of sols towards electrolytes, both the concentration as well as the amount of peptising agent are important factors.

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[1] Pauli and Matula: Kolloid-Z. 21, 49 (1917).

(2) It is shown in the case of aluminium hydroxide suspensions, that with benzoic, acetic and propionic acids, the stability of the suspension depends both on the concentration of the hydroxide as well as on the amount of the acid present.

(3) With increase in concentration of the acid, the stability gradually increases to a maximum. With the same purity of the suspension, the stability decreases with dilution. This is in agreement with the law that the greater the concentration of a sol, the greater is its stability towards electrolytes.

My best thanks are due to Professor N. R. Dhar for his interest in this work.

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April 20, 1924.

THE THERMAL DECOMPOSITION OF METHANE

BY R. C. CANTELO

That methane could be formed synthetically by direct union of carbon and hydrogen was first demonstrated by Bone and Jerdan in 1897.[1] They heated pure sugar carbon in a current of dry hydrogen in a porcelain tube at 1200°C. and obtained about 1% of methane in the products. Later Bone and Coward[2], in order to confirm these results, heated purified sugar charcoal as before in a stream of pure hydrogen and from 0.34 g. of carbon heated at 1020-1070°C., they obtained 14.25 cc. of CH_4. This they claimed, confirmed the synthesis of methane at this temperature. Berthelot[3] attempted the same synthesis, but could obtain no methane. He attributed the methane obtained by Bone and Jerdan to impurities contained in the carbon used by the English chemists.

Sabatier and Senderens[4] by the action of hydrogen upon an intimate mixture of carbon and nickel obtained by reduction of its oxide at 250-300°C., ascertained that methane was formed at 250°C., but at the same time there was a formation of water vapor. After some time, however, the hydrogen ceased to react. The same chemists found no methane when the temperature was raised to 400°C.

Mayer, Henseling, Altmayer and Jacoby[5], experimenting with the effects of catalysts on the synthesis of methane, found nickel, cobalt and iron efficient in the order given. Pring and Fairlie[6] found that below 1000°C. and at atmospheric pressure, the reaction was extremely slow, even in the presence of a catalyst like platinum.

The reaction then began to receive attention from the other side, and several investigations on the decomposition of methane were undertaken. Bone and Coward[7], working at temperatures between 500°C. and 1200°C. declared that the rate of decomposition was inappreciable at temperatures below 700°C. unless a very large surface was exposed by packing with porous material. They believed decomposition to be largely a surface effect and, as such, affected by the deposit of carbon. Packing with quicklime resulted in a more rapid attainment of equilibrium. An analysis of the products from an hour's heating at 1030°C. revealed the decomposition of all but 0.7% of methane. The deposit of carbon was hard and lustrous.

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[1] J. Chem. Soc. 71, 42 (1897).

[2] J. Chem. Soc. 93, 1975 (1908).

[3] Ann. chim. phys. (8), 6, 183 (1905).

[4] Bull. (4), 1, 107 (1907).

[5] J. Gasbel, 52, 166, 238, 305.

[6] J. Chem. Soc. 89, 1591 (1906), 99, 1796 (1911).

[7] J. Chem. Soc. 93, 1197 (1908).

Slater[1] carried out an investigation to determine whether the rate of dissociation of methane depended upon the physical and chemical nature, as well as on the amount, of the heating surface exposed to the gas. On the basis of the amount of dissociation in an empty tube it was found that silica, magnesia, alumina and baryta slowed up the reaction, while quicklime, copper, carborundum, graphite, charcoal and iron accelerated the decomposition. Heated with powdered iron at 910°C. for ten minutes, a gas analyzing 99.4% methane gave a product that was 73.1% hydrogen. Slater concluded that each substance exerts a specific influence on the rate of decomposition which therefore depends upon the nature of the substance as well as on the amount of the heating surface.

As a result of a later investigation Pring and Fairlie[2] found that high pressure hastens the attainment of equilibrium, and that rapid cooling prevents the formation of much ethylene. Under a pressure of 30-50 atmospheres, equilibrium was reached at the end of 2 hours with a temperature of 1200-1300°C., and at the end of 15 minutes at 1400°C., with or without a catalyst. The reaction was still more rapid at other pressures.

Mayer and Altmayer[3] studied the methane equilibrium in the presence of cobalt and nickel catalysts. Using the method of Haber these investigators obtained the equation:

$$21.1+\frac{18{,}507}{T}-5.9934\ \log_e T-0.002936\ T$$
$$=R\log_e \frac{p_{CH_4}}{p^2_{H_2}}$$

They then state: "Durch beliebiges Einsetzen der Temperaturwerte T können wir die Gleichgewichtskonstante p berechnen. Hieraus sind mit Hilfe einer quadratischen Gleichung die Gleichgewichtswerte für CH_4 und H_2 zu ermitteln."

Their calculated equilibrium values for temperatures from 600°C. to 800°C. are here reproduced.

TABLE I

Temperature °C.	% CH_4	% H_2
600	31.68	68.32
650	19.03	80.97
700	11.07	88.93
750	6.08	93.92
800	4.41	95.59
850	1.59	98.41

They attack the observation of Bone and Jerdan[1] that in their experiments upon the synthesis of methane at 1200°C. they obtained 1-2% methane. The above results seem to indicate that methane cannot be formed from carbon and hydrogen at 1200°C.

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[1] J. Chem. Soc. 109, 160 (1916).

[2] J. Chem. Soc. 101, 91 (1912).

[3] Ber. 40, 2134 (1907).

The following thermodynamical treatment of the equilibrium $C+2H_2 \rightleftarrows CH_4$ while considerably simplified, is essentially that used by Mayer and Altmayer. The van't Hoff Isochore is—

$$\frac{d \log_e K_p}{dT} = -\frac{H_p}{RT^2}$$

Integrated

$$\log_e K_p = \frac{H_p}{RT} - \int \frac{1}{RT} \cdot dH + \text{const.} \qquad (1)$$

$$= \frac{H_p}{RT} - \int \frac{(C_1-C_2)}{RT} \cdot dT + \text{const.} \qquad (2)$$

where C_1 is the heat capacity of the reactants and C_2 that of the products. Rearranging

$$RT \log_e K_p = H_p - T\int \frac{(C_1-C_2)}{T} dT + T.\text{const.} \qquad (3)$$

Again if Φ_1 is the thermodynamic potential of the gaseous system CH_4 and Φ_2 that of the system $2H_2$ formed from the first one at constant temperature and pressure, then

$$(\Phi_1-\Phi_2)_{Tp} = RT \log_e K_p - RT\Sigma v_1 \log_e p_1 \qquad (4)$$

Substituting equation (3) in (4) gives

$$(\Phi_1-\Phi_2)_{T,p} = H_p - T\int \frac{(C_1-C_2)}{T} dT + T.\text{const} - RT\Sigma v_i \log_e p_i \qquad (5)$$

For equilibrium $\Phi_1 = \Phi_2$ whence $T.\text{const.} = -H_p + T \int \frac{(C_1-C_2)}{T} .dT + RT\Sigma v_i \log_e p_i$ (6)

Since both C_1 and C_2 are functions of T, it is possible to express (C_1-C_2) in the form $\alpha+\beta T+\gamma T^2+ \ldots$

whence equation (6) becomes

$$T.\text{const} = -H_p + T\int \frac{\alpha+\beta T+\gamma T^2}{T} . dT + RT \log_e K_p \qquad (7)$$

or

$$T.\text{const} = -H_p + \alpha T \log_e T + \beta T^2 + \tfrac{1}{2}\gamma T^3 + RT \log_e K_p \qquad (8)$$

In this equation H_p represents the number of calories evolved when the products of the reaction are restored to the temperature of the reactants, i.e. H_p represents the heat effect that would attend the reaction if it took place isothermally at the initial temperature. H_p, the heat of formation of methane is equal to 18,900 calories per gram molecular weight.[1]

The mean specific heat of carbon per atomic weight between O and T absolute is given by the equation[2]

$$C_m = 2.0994 + 0.001736\ T.$$

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[1] Hodgman and Lange: "Handbook of Chemistry and Physics," 9th ed., p. 384.

[2] Ann. Physik. (4), **14**, 328 (1904).

The specific heat per mol of hydrogen is

$$6.5+0.0006\ T.$$

The specific heat per mol of methane, according to the determined value of Wüllner,[1] is 9.106.

Accordingly $\alpha=2.0994+13-9.106=5.9934$

$\beta= .001736+.0012=0.002936$

Equation (8) above applied to the methane equilibrium may be written—

$$T\ \text{const}=-18{,}900+5.9934\ T\log_e T+0.002936\ T^2 + RT\log_e \frac{p_{CH_4}}{p^2_{H_2}} \qquad (9)$$

This equation differs from that of Mayer and Altmayer solely in the first term. The writer has used for H_p, the heat of the reaction for ordinary temperatures; Mayer and Altmayer in place of this term have used the heat of the reaction calculated for 0°C.

There remains the determination of the constant of integration. Mayer and Altmayer determined this constant from their experimental results. They attempted both the decomposition and synthesis of methane in the presence of the catalysts nickel and cobalt. From their results they obtain the constant $=21.1$. It is, however, very doubtful that this is the correct value. A critical examination of their results reveals the fact that in no case was equilibrium actually reached. For example at 536°C., in experiments on the synthesis of methane by nickel as catalyst we find the following divergent values for $\log K_p$—0.08061, 0.25239, 0.18290, 0.45200, 0.28302, 0.17747, 0.13888. Other experimental results for differing temperatures show similar disagreements.

The constant, however, calculated from their results varies for all the experiments between 18.8 and 22.0. This is quite possible as an inspection of their final equation shows.—

$$\text{Const.}\ T=-18{,}507+5.9934\ T\log_e T+0.002936\ T^2+RT\log_e \frac{p_{CH_4}}{p^2_{H_2}}$$

A variation of 100% in the value of $\log_e \dfrac{p_{CH_4}}{p^2_{H_2}}$

produces a difference of only 5% in the value of the constant. It is interesting to note here that von Wartenburg[2] attempted to use the values of K_p obtained by Mayer and Altmayer in an application of the Nernst Heat Theorem to the methane equilibrium and he found that the calculated and observed values of T were not in agreement.

Fortunately the Nernst approximation formula enables one to obtain a "fairly accurate" value for K_p, from which it will be possible to obtain some idea of the order of the constant of integration.

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[1] Values are those from Mayer and Altmayer's paper.

[2] Z. physik. Chem. 63, 269 (1908).

The Nernst formula[1] is

$$\log K = \frac{H_p}{4.571\ T} + \Sigma v\ 1.75 \log T + \Sigma vC$$

where H_p is the heat developed at ordinary temperatures, Σv represents the volume changes and ΣvC a summation of constants.

If we apply the approximation to the equilibrium at 600°C. the equation becomes

$$\log K_{600} = \frac{+\ 18,900}{4.571 \times 873} - 1.75 \log 873 - 0.7$$

whence $K_{600} = 0.077$.

In the same way the results given in Table II were calculated.

TABLE II

Temperature	$K_p = \frac{p_{CH_4}}{p^2_{H_2}}$
600	0.077
650	0.039
700	0.021
750	0.012
800	0.007
850	0.003
900	0.003
1000	0.0015

The constant of integration of equation (9) may now be obtained by substituting in it $K_{600} = 0.077$ whence

$873 \times \text{const.} = -18,900 + 5.9934 \times 873 \times 2.3 \log 873$
$+ 0.002936 \times 873 + 2 \times 873 \times 2.3 \log 0.077$
whence const. = 16.

Let us now calculate K_{600} using in turn the constants 21 and 16.

$873 \times 21 = -18,900 + 35,250 + 2230 + 2 \times 873 \times 2.3 \log K_p$
whence $\log K_p = \bar{1}.9426$
whence $K_p = .87$ where const. = 21.

Again
$873 \times 16 = -18,900 + 35,250 + 2230 + 1746 \times 2.3 \log K_p$
whence $\log K_p = \bar{2}.8480$
whence $K_p = .07$ where const. = 16.

It is evident, therefore, that the equilibrium concentrations calculated by Mayer and Altmayer (Table I) are in error. Table III contains the equilibrium concentrations of CH_4 and H_2, calculated by the writer using the values for K_p given in Table II.

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[1] Vide Lewis' "System of Physical Chemistry," 1st ed. Vol. II, p. 388.

TABLE III

Temperature °C.	% CH_4	% H_2
600	6.9	93.1
650	3.5	96.5
700	2.0	98.0
750	1.0	99.0
800	0.5	99.5
850	0.4	99.6
900	0.4	99.6
1000	0.2	99.8

The method of calculation of the values given in Table III is evident from the following example for temperature = 600°C.

$$C + 2\,H_2 \rightleftarrows CH_4$$

Let 2x be number of mols of hydrogen in the equilibrium mixture

Then 1 − x = number of mols of methane

whence $$K_p = \frac{p_{CH_4}}{p^2_{H_2}} = \frac{\left(\frac{1-x}{1+x}\right) \times 1}{\left(\frac{2x}{1+x}\right)^2 \times 1}$$

whence $x = 0.87$

so that the percentage of hydrogen $= \frac{2x}{1+x} \cdot 100 = 93.1$

The values given in Table II indicate that even at as low a temperature as 700°C. methane should be decomposed almost completely into carbon and hydrogen, and that only a trace of methane could be present at 1000°C.

These conclusions are of considerable interest when applied to the problem of the manufacture of carbon black from natural gas, which is chiefly methane. That an attempt should be made to manufacture carbon black from the thermal decomposition of natural gas is not surprising, for both the products carbon and hydrogen have considerable economic value, while in the production of carbon, in particular, the thermal decomposition process would be competing with an established method of low efficiency.

II. Carbon Black[1]

The various carbons used in the industries are produced by one of the following methods:

1. Liberation by direct contact of flame on depositing surface. The product is usually known as carbon black.

2. Production by combustion of oil, tar, or other liquid or solid carbonaceous material with insufficient air. The soot so formed slowly settles on the floors and walls of collecting chambers. The product is usually known as lampblack.

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[1] Information included here taken from U. S. Bur. of Mines Bull. 192.

3. Carbonization of solids, usually refuse, and subsequent mechanical reduction to a fine state of subdivision.

4. Thermal Decomposition.

The blacks yielded by the different processes possess different physical and, sometimes, chemical properties. As a result, each black has its specific use and usually cannot be substituted for another. These substances are not pure carbon, but usually contain hydrocarbons as well as other organic substances and mineral matter.

The recovery of carbon black, as manufactured from natural gas under present processes, varies between 2 and 3% and is in direct proportion to the content of ethane. For the gases richer in the higher hydrocarbons, not only is the actual quantity of carbon obtained greater, but the percentage recovery increases as well. The low efficiency has led to the belief that the present processes are wasteful ones, and this fact, taken together with the menace of steadily declining supplies of available natural gas, in turn has produced considerable agitation for laws against the use of natural gas in this manner, for the manufacture of carbon black. Absolute prohibition of the industry in one state and its close regulation in several others have resulted from these conditions. Irrespective of the merits of the question, it is evident that if the thermal decomposition process can offer a greater yield of a similar quality of carbon, these other processes will disappear with the substitution of one which will afford the conservationists less opportunity and desire of attacking.

Hydrogen, the other product of the reaction, also has an economic value. The decomposition process for its production seems to be commercially practical, for the only plant at present operating under this process produces hydrogen alone and does not even collect the carbon formed.

A number of methods for the thermal decomposition of natural gas have been patented. In most of them the process takes place at a temperature of 1,200°C. or over. While as high as 40% of the theoretical yield has been obtained in this way, a *salable* grade has not yet been made by this means.

If the carbon after formation is allowed to remain in the heated zone too long, the particles become agglomerated and a grey variety of amorphous carbon results. In one method this is overcome by providing a cold surface for the collection of the carbon immediately after its liberation, while other processes rely upon the rapid expansion of the decomposing gases to sweep the carbon out of the heated zone. At any rate, the production of a black suitable for use in the rubber industry ought to be capable of attainment by one of these processes. The opinion of an expert on the future of the process may be quoted here. R. O. Neal of the U. S. Bureau of Mines says: "Thermal decomposition probably offers the most promising method of increasing the quality of black from natural gas. The present methods are destructive to the apparatus—a defect that can undoubtedly be overcome—and the resultant product contains grit or adamantine matter, is grayish and contains some volatile matter."

The above, taken in conjunction with the calculated results given in Table III, suggests the idea of a low temperature (i.e. at 600-800°C.) decomposition of natural gas. The difficulty of such a process lies, of course, in the extremely slow velocity at which equilibrium is reached between methane and its decomposition products. Obviously, such a low temperature decomposition would require the use of a catalyst; and in the third part of this paper, the results are given of experiments which were carried out in the writer's laboratory, in the search for a suitable catalyst.

One other question may be considered at this point, viz: does the equilibrium between methane and hydrogen represent the lowest potential energy possible, that is, might there not be also the simultaneous occurrence of other reactions?

Methane might decompose in any one of the following ways:

(1) $CH_4 \rightleftarrows C+2H_2$

(2) $2CH_4 \rightleftarrows C_2H_4+2H_2$

(3) $2CH_4 \rightleftarrows C_2H_2+3H_2$

However, if the equilibrium constants are calculated by the Nernst formula the following values are obtained:

	K_{600}	K_{750}	K_{900}
Reaction (1)	13.0	83.4	330
Reaction (2)	1×10^{-7}	1×10^{-5}	4×10^{-4}
Reaction (3)	1.9×10^{-11}	1×10^{-7}	6×10^{-5}

Evidently an entirely negligible amount of ethylene and acetylene can be expected.

From 1000 cu. ft. of methane there would be obtained theoretically by decomposition at 600°C:

$1000\times(1.87)=1870$ cu. ft. of mixed hydrogen and methane, containing:

$1870\times.069=130$ cu. ft. of methane.

$1870\times.931=1740$ cu. ft. of hydrogen,

i.e. 870 cu. ft. of methane should be decomposed, and should yield 27 pounds of carbon.

While these figures would not be reached in any practical operation involving this process, it is interesting to compare the theoretical yield of carbon with those actually obtained in ordinary lampblack and carbon black plants. In the latter case the value never exceeds 1.5 pounds.

Should a successful catalyst for the decomposition of methane into carbon and hydrogen be discovered, there will still remain the difficulty of preventing the carbon from depositing upon the catalyst. This, however, is a mechanical difficulty which human ingenuity can no doubt overcome.

III. Experimental Part

The apparatus used in making the experiments which will be described later was of the simplest. The heating unit was a cylindrical electric furnace with a lamp bank in circuit for regulating the current to give any desired temperature. The reaction tube was of fused silica. The gasometer containing the methane was connected by means of two large calcium chloride tubes with the reaction tube. The gas, accordingly, passed from the gasometer through the U-tubes and then through the reaction tube, after which it passed through another pair of calcium chloride tubes into a second gasometer. These gasometers were large glass bottles fitted with large separatory funnels and drains, whereby the pressure was regulated. The admission of water through the funnel of the first bottle increased the pressure on the contained gas, and the opening of the drain of the second bottle removed water and lowered the pressure. By proper regulation gas could be transferred from one bottle to the other at any desired rate. The calcium chloride tubes were provided to keep the gases in the reaction tube free from water.

The methane used was obtained by heating together a mixture of sodium acetate and soda lime; the following reaction taking place:

$$CH_3COONa + NaOH \longrightarrow Na_2CO_3 + CH_4.$$

Methane prepared by this method is not pure and contains considerable hydrogen. This, however, was of little consequence for our experiments, as we are concerned solely with an equilibrium mixture, one of the constituents of which is hydrogen.

The experimental method was as follows: The furnace was brought first up to the required temperature. Nitrogen was passed at a rapid rate through the calcium chloride tubes and the reaction tube containing the catalyst, for 20 minutes, and following this the two gasometers were connected in their proper positions and the methane passed through the reaction tube at the desired rate. After about 3 litres of methane had passed through the tube, the experiment was stopped, the gasometers disconnected from the furnace, and the resulting gas mixture was analyzed.

The question will arise as to whether the nitrogen will influence the rate of the reaction and the final equilibrium state. Naturally, its presence by decreasing the partial pressures of methane and hydrogen will reduce the velocity at which equilibrium is reached, but the presence of an efficient catalyst would render this effect negligible. It will, however, affect the final equilibrium state. If we examine the equilibrium expression for this reaction, viz: $K_p = \frac{p^2_{H_2}}{p_{CH_4}}$, it is evident that the presence of nitrogen at an appreciable partial pressure tends to decrease the value of the expression on the right hand side of the equation (assuming no reaction takes place). Therefore, to restore the equilibrium value of the ratio K_p, a further dissociation of methane must take place. The presence of nitrogen, then, favors the dissociation.

The analyses given below have been calculated to a nitrogen-free basis, in order to compare the methane and hydrogen contents with those given in Table III for the equilibrium percentages of these gases.

Experimental Results.

I. Temperature 600°C.

Run No. 1—No catalyst.

Rate—20 cc. per minute.

Volume CH_4 used—2700 cc. Volume of resulting gas—2650 cc.

	Analyses Original	Final
CH_4	91.2	88.9
H_2	6.9	8.7
C_2H_4	0.6	1.2
CO	1.3	0.9
CO_2	0.0	0.3
O_2	0.0	0.0

Run No. 2—CaO used as catalyst.

Space Velocity—58 litres gas per litre catalyst space per hr.

Volume of CH_4 used—3400 cc. Volume of resulting gas—3400 cc.

	Analyses Original	Final
CH_4	85.0	83.5
H_2	12.0	14.4
C_2H_4	2.1	1.1
CO	0.6	1.1
CO_2	0.0	0.0
O_2	0.3	0.0

Run. No 3—Bone black as catalyst.

Space Velocity—42 litres gas per litre of catalyst space per hour

Volume of CH_4 used—2550 cc. Volume of resulting gas—2700 cc.

	Analyses Original	Final
CH_4	85.5	80.0
H_2	13.1	17.8
C_2H_4	1.4	0.2
CO	2.0	0.0
CO_2	0.0	0.0
O_2	0.0	0.0

Run No. 6—Cu-CuO as catalyst.

No increase in volume was obtained. Final gas was not analyzed.

Run No. 7—Asbestos impregnated with Ni-NiO as catalyst.

Space velocity—41 litres gas per litre of catalyst space per hour.

Volume of CH_4 used—3100 cc. Volume of resulting gas—3400 cc.

	Analyses	
	Original	Final
CH_4	88.0	81.2
H_2	10.3	17.2
C_2H_4	1.7	0.0
CO	0.0	0.0
CO_2	0.0	1.6
O_2	0.0	0.0

Run No. 8—Asbestos impregnated with Ni-NiO as catalyst.

Space velocity—46 litres gas per litre of catalyst space per hour.

Volume of CH_4 used—3500 cc. Volume of resulting gas—3800 cc.

	Analyses	
	Original	Final
CH_4	88.0	81.3
H_2	10.3	17.7
C_2H_4	1.7	0.0
CO	0.0	0.5
CO_2	0.0	0.5
O_2	0.0	0.0

2. TEMPERATURE 700°C.

Run No. 11—No catalyst.

Rate—30 cc. per minute.

Volume of methane used—4050 cc. Volume of resulting gas—4000 cc.

	Analyses	
	Original	Final
CH_4	95.6	87.6
H_2	1.9	10.4
C_2H_4	1.4	0.7
CO	1.1	1.0
CO_2	0.0	0.3
O_2	0.0	0.0

Run No. 9—Asbestos impregnated with Ni-NiO as catalyst.

Space velocity—43 litres of gas per litre of catalyst space per hour.

Volume of CH_4 used—3300 cc. Volume of resulting gas—4150 cc.

	Analyses	
	Original	Final
CH_4	91.0	56.0
H_2	8.4	43.2
C_2H_4	0.4	0.0
CO	0.2	0.8
CO_2	0.0	0.0
O_2	0.0	0.0

Run No. 10—Catalyst as in Run 9.

Space Velocity—43

Volume of CH_4 used—3500 cc. Volume of resulting gas—4000 cc.

Analyses

	Original	Final
CH_4	91.0	62.1
H_2	8.4	37.9
C_2H_4	0.4	0.0
CO	0.2	0.0
CO_2	0.0	0.0
O_2	0.0	0.0

3. TEMPERATURE 760°C.

Run No. 12—No catalyst.

Rate—30 cc. per minute.

Volume of CH_4 used—2700 cc. Volume of resulting gas—2900 cc.

Analyses

	Original	Final
CH_4	92.9	85.7
H_2	6.5	12.2
C_2H_4	0.0	0.6
CO	0.0	0.3
CO_2	0.6	0.8
O_2	0.0	0.4

Run No. 13—Asbestos impregnated with Fe_2O_3-Fe.

Space velocity—30 litres gas per litre of catalyst space per hour.

Volume of CH_4 used—3700 cc. Volume of resulting gas—3950 cc.

Analyses

	Original	Final
CH_4	89.5	81.4
H_2	9.1	13.8
C_2H_4	1.4	0.0
CO	0.0	2.2
CO_2	0.0	2.5
O_2	0.0	0.0

Run No. 14—Silica gel as catalyst.

Space velocity—21 litres gas per litre of catalyst space per hour.

Volume of CH_4 used—3300 cc. Volume of resulting gas—3400 cc.

Analyses

	Original	Final
CH_4	89.5	83.5
H_2	7.0	14.2
C_2H_4	3.5	1.6
CO	0.0	0.0
CO_2	0.0	0.7
O_2	0.0	0.0

Run No. 15—Asbestos impregnated with MnO_2

Space velocity—20 litres of gas per litre of catalyst space per hour.

Volume of CH_4 used—3400 cc. Volume of resulting gas—3400 cc.

Analyses

As there was no increase in volume during this experiment an analysis of the resulting gas was not made.

4. TEMPERATURE 780°C.

Run No. 16—Asbestos impregnated with Ni-NiO as catalyst.

Space velocity—52 litres of gas per litre of catalyst space per hour.

Volume of CH_4 used—2700 cc. Volume of gas obtained—4250 cc.

Analyses

	Original	Final
CH_4	83.5	23.6
H_2	7.9	71.9
C_2H_4	4.0	0.0
CO	2.4	1.9
CO_2	0.9	2.5
O_2	1.3	0.0

IV. Conclusion

An examination of the above experimental results shows that the majority of the contact materials used produced some catalytic effect upon the reaction. The effect of the Ni-NiO catalyst is especially noticeable, and the catalytic action of this material is such that it seems highly probable that complete equilibrium may be obtained at 780°C., using this catalyst and a smaller space velocity.

Experiments are now in progress in this laboratory with a view to determining the equilibrium concentrations of methane and hydrogen in the way indicated above. From such equilibrium concentrations, the equilibrium constant, K_p, may be determined for the methane equilibrium, and the value so obtained compared with that calculated by means of the Nernst approximation.

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A REVISION OF THE ATOMIC WEIGHT OF GERMANIUM.*

I. THE ANALYSIS OF GERMANIUM TETRACHLORIDE.

BY GREGORY PAUL BAXTER AND WILLIAM CHARLES COOPER, JR.

Introduction

The atomic weight of germanium has been determined by two investigators. Winkler,[1] the discoverer of germanium, analyzed the tetrachloride and obtained the value 72.5. Quite recently, in a very concordant series of experiments, Müller[2] converted weighed amounts of potassium fluorgermanate into potassium chloride, and found in this way the atomic weight of germanium to be 72.42.

Because germanium has recently become available in moderate quantities and because the tetrachloride may be readily prepared and purified by fractional distillation, by methods perfected in this laboratory for handling other volatile mineral halides, notably the chlorides and bromides of silicon,[3] titanium,[4] and boron,[5] we have undertaken the analysis of germanium tetrachloride. The value which we have obtained is not at all in agreement with that of Müller and is considerably higher even than that of Winkler.

Purification of Materials

Reagents

Water. Ordinary distilled water was twice redistilled, once from alkaline permanganate, and once from very dilute sulfuric acid. The condensers were block tin tubes, fitted to Pyrex flasks with constricted necks which served as stills. The connection was made by a water seal, no cork or rubber being used. The water was collected in Pyrex flasks, generally just previous to use.

Nitric Acid. Concentrated C. P. nitric acid was distilled through a quartz condenser, the first two-thirds, as well as the last tenth being rejected. if necessary, the fractional distillation was continued until the product was free from chloride.

Silver. This substance was prepared by standard methods. These consisted in brief of the following processes: double precipitation as chloride, followed by reduction with alkaline sugar solution, fusion of the metal on charcoal, solution in nitric acid and repeated crystallization of silver nitrate, precipitation with ammonium formate, fusion on pure lime, electrolytic transport, fusion on pure lime in hydrogen, etching, drying in a vacuum at 500°.

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*Contribution from the T. Jefferson Coolidge Jr. Memorial Laboratory, Harvard University.

[1] Winkler: J. prakt. Chem., (2), **34**, 177 (1886).

[2] Müller: J. Am. Chem. Soc., **43**, 1085 (1921).

[3] Baxter, Weatherill and Scripture: Proc. Am. Acad., **58**, 245 (1923).

[4] Baxter and Fertig: J. Am. Chem. Soc., **45**, 1228 (1923).

[5] Baxter and Scott: Science, (2) **54**, 524 (1921); Proc. Am. Acad., **59**, 21 (1923).

Details of these processes may be found in earlier papers from the Harvard Chemical Laboratories.[1] Recent work by Baxter and Parsons[2] and Baxter[3] as well as earlier investigations have shown that these processes yield a product of adequate purity.

Sodium Hydroxide. This substance was prepared by metathesis from barium hydroxide and sodium carbonate, both of which had been recrystallized until practically free from chloride. The solution was freed from precipitate by centrifugal settling and after evaporation in platinum dishes was allowed to crystallize. Since the product was found to contain a small amount of chloride it was recrystallized several times in platinum dishes until the chloride had been completely removed.

Nitrogen. Nitrogen was prepared by the Wanklyn process. Air was charged with ammonia and passed over hot copper catalyst. The excess of ammonia was removed in wash bottles containing dilute sulfuric acid, and the gas was further purified and dried by passing through towers filled with beads moistened with silver nitrate, potassium hydroxide and concentrated sulfuric acid and through a tube containing resublimed phosphorus pentoxide. The hydrogen formed by decomposition of part of the excess of ammonia was not removed. The apparatus was constructed wholly of glass, with either fused or ground connections, the latter being lubricated with concentrated sulfuric acid.

Chlorine. This gas was drawn in part from a tank of liquid material, in part it was prepared from concentrated hydrochloric acid and manganese dioxide. The chlorine was scrubbed with water and dried with concentrated sulfuric acid and finally phosphorus pentoxide, in an apparatus constructed wholly of glass.

Extraction of Germanium from Zinc Oxide Residues

We are very greatly indebted to the New Jersey Zinc Company for the generous gift of one hundred and twenty-five pounds of germaniferous zinc oxide, containing approximately 0.25 per cent of germanium dioxide. In extracting the germanium we followed essentially the procedure described by Dennis and Papish[4] by which the germanium and arsenic are first separated together. At the time the improved method of Dennis and Johnson[5] had not been described. On the other hand the final separation of the germanium from the arsenic was effected by fractional distillation of the chlorides in vacuum, instead of by distillation from hydrochloric acid solution in a current of chlorine, as practised by Dennis and his collaborators. Because of the relatively large difference in boiling points, 43°, this separation is comparatively rapid.

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[1] See especially Richards and Wells: Pub. Carnegie Inst., No. 28, 16 (1905).

[2] Baxter and Parsons: J. Am. Chem. Soc., 44, 577 (1922).

[3] Baxter: J. Am. Chem. Soc., 44, 591 (1922).

[4] Dennis and Papish: J. Am. Chem. Soc., 43, 2131 (1921). See also Buchanan: J. Ind. Eng. Chem., 8, 585. (1916); 9, 661 (1917).

[5] Dennis and Johnson: J. Am. Chem. Soc., 45, 1380 (1923).

The crude zinc oxide was dissolved in a large flask in a considerable excess of hydrochloric acid, and the solution was distilled until the volumes of the distillate was about twice the volume of the residue. After the acidity of the distillates had been brought to 6 normal by the addition of sulfuric acid, they were saturated with hydrogen sulfide. The precipitated sulfides of arsenic and germanium were washed until nearly free from chloride, with 5 normal sulfuric acid which had been saturated with hydrogen sulfide. Drying at 110° followed.

A large portion of the arsenic was next removed by roasting the sulfides in a current of air at about 500°. Dennis and Papish[1] state that about 90 per cent of the arsenic is eliminated in this way. In the earlier experiments the sulfides were contained in a copper boat placed inside a glass tube which could be heated electrically. During the roasting a fairly rapid current of dry air was passed through the tube. Owing to extensive contamination of the product by copper oxide, the copper boat was later replaced by one of nickel steel.

The crude germanium dioxide was next finely powdered and subjected to a second roasting in a current of dry air at about 650°, while contained in an alundum boat inside a quartz tube. Material evaporating during this treatment and the following one was collected in traps connected with the outlet of the silica tube. After the roasting the air was replaced by a current of pure dry electrolytic hydrogen and the temperature, after being maintained at redness for some time, was ultimately raised to approximately 1000°. Most of the reduced material melted and coalesced at this temperature and at the same time a very considerable black sublimate consisting chiefly of arsenic was formed. About one hundred and thirty grams of crude germanium metal were thus secured.

Preparation and Distillation of Germanium Tetrachloride

Germanium tetrachloride was next prepared by heating the metal in a current of chlorine, purified and dried as described on page 1050. The chlorine train was connected through a ground joint with a hard glass tube in which the metal was loosely packed between asbestos plugs. This tube was also connected with a supply of dry atmospheric nitrogen prepared as described. The tube containing the germanium was inclined downward and connected at its lower end by means of a ground joint with two condensing bulbs in series, one cooled with ice and salt, the second with alcohol-carbon dioxide mixture.

The nitrogen train and germanium tube were swept out with nitrogen for many hours. At the same time the chlorine train was swept out through a side tube. Chlorine was then admitted to the reaction tube and the germanium was heated electrically by means of a sleeve wound with resistance wire. After a considerable quantity of the chloride had been formed, the apparatus became choked so badly that the experiment was discontinued. The contents

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[1] Dennis and Papish: J. Am. Chem. Soc., 43, 2139 (1921).

of the hard glass tube were washed with water, dried and ignited in hydrogen and the experiment was repeated with similar apparatus. In all about one hundred cubic centimeters of chloride were prepared.

The chloride at this point contained free chlorine. It also was turbid owing in part at any rate to suspended copper salts, for the original metal was contaminated with copper as stated on page 1051. It presumably contained hydrogen chloride and either germanic acid or oxychloride owing to some contact with the moisture of the air. Subsequent examination showed it to contain arsenic trichloride in considerable proportions, and traces of tin and antimony. Silicon might have been introduced in the reaction with chlorine in the hard glass tube but we were unable to discover this impurity. In the formation of boron halides[1] this is a serious difficulty. The boiling points of the chlorides mentioned above and some others are given in the following table together with the effect on the observed atomic weight of germanium of a proportion of 0.1 per cent of each substance alone.

TABLE I

Boiling Points of Inorganic Chlorides

	Boiling point degrees	Effect of 0.1% on atomic weight of Ge
HCl	−83	−0.070
CCl_4	76.5	−0.061
$SiCl_4$	58	−0.045
$TiCl_4$	136	−0.025
$GeCl_4$	86.5	
$SnCl_4$	114	+0.048
VCl_4	154	−0.021
PCl_3	76	−0.032
$AsCl_3$	130	+0.028
$SbCl_3$	223	+0.049

The germanium tetrachloride was now purified by fractional distillation in a fashion very similar to that used in purifying the halides of silicon, titanium and boron in this laboratory.[2] The two lots of germanium tetrachloride were combined in a single glass bulb (A, Figure 1) in which a few cubic centimeters of mercury had been placed. The bulb was connected with a side tube *a* for exhausting and with a special joint *b* by means of which the bulb could be connected later with additional systems, without breaking the vacuum. In the vertical view of the special joint[3] the sealed-in capillary *m* is closed at the end and is scratched with a file at several points to facilitate breaking. To break the joint the closed tube of glass weighted with mercury *n* is allowed to strike the capillary with some force. The bulb was exhausted

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[1] Wöhler and Deville: Ann. chim. phys., (7) 6, 296 (1895).

[2] Loc. cit., page 1049.

[3] Baxter, Weatherill and Scripture: Proc. Am. Acad. 58, 250 (1923).

by means of an efficient water pump through a tube containing sodium hydroxide, while at the same time it was cooled with ice and water to lower the vapor pressure of the germanium tetrachloride. Even under these conditions the tetrachloride boiled gently, thus flushing out the air in the bulbs, together with a part of the chlorine and the hydrochloric acid formed by contact with moisture in the air. After the boiling had proceeded for a short time the tube *a* leading to the pump was sealed off. In order to remove the remainder of the chlorine the tetrachloride and the mercury were emulsified by shaking, and allowed to stand for some time.

Next the bulb A, containing the tetrachloride, was connected through the special joint with another bulb B attached through a vertical tube to a fractionating column *e* filled with glass pearls and jacketed with a large glass tube. Beyond the fractionating column were another similar bulb C and fractionating column *g* terminating in a special joint *i*. The bulbs B and C and the fractionating columns were exhausted by a Gaede mercury pump through the capillary *h* which was sealed while the pump was operating. Communication between A and B was now made by breaking the special joint *b* and the tetrachloride was largely distilled from A and B by chilling B with salt and ice. After three-quarters of the liquid had distilled the volatility of the remainder became so much less that only by surrounding A with hot water could the distillation be continued. As subsequently found this was due to the concentration of the less volatile arsenic trichloride. The bulb A containing a small amount of liquid together with a residue of mercury and mercurous chloride was detached by sealing the capillary *c*. In the next distillation from B to C the fractionating column *e* was first chilled with ice water. The still B was then surrounded with warm water and the bulb C was chilled with salt and ice. Under these conditions a very efficient fractionation took place with refluxing throughout the fractionating column but without choking. When the residue in B had been reduced to about ten cubic centimeters the volatility was obviously so much less than that of the main portion that the apparatus was divided by sealing the capillary *f*.

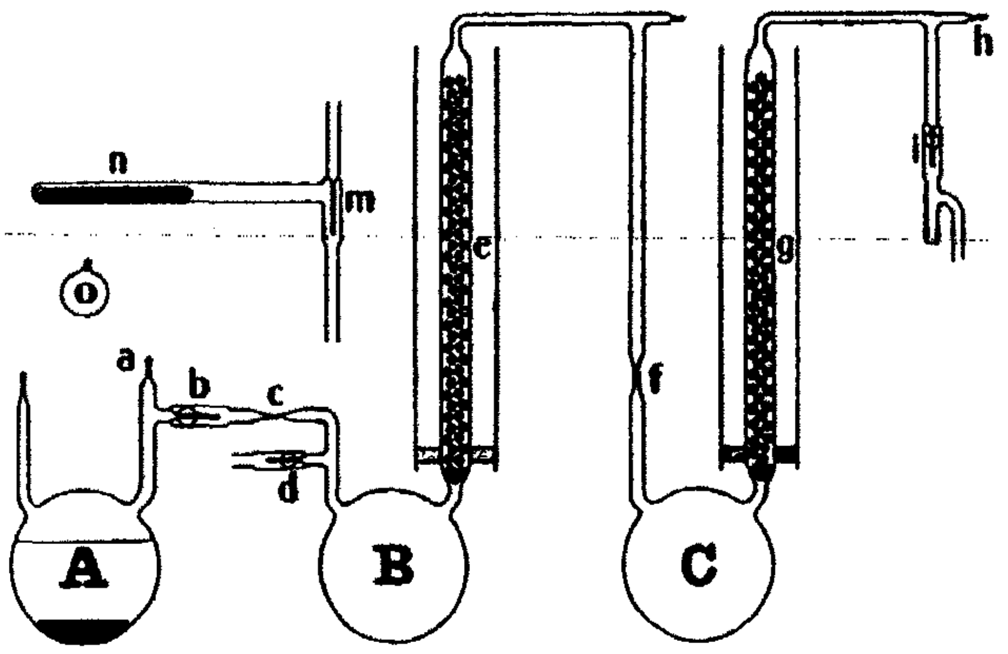

Fig. 1

The less volatile residue in B was now fractionated into five exhausted bulbs attached through the special joint *d*. These fractions, 40, 41, 42, 43, 44, (Figure 3) were hydrolyzed and found by treatment with hydrogen sulfide to consist largely of arsenic. Spectroscopic examination of the sulfide fractions on graphite electrodes with a Féry quartz spectrograph indicated also the presence of traces of tin and antimony.

In the next distillation from C to a similar system attached through the special joint *i*, difficulty was experienced in condensing a light fraction in a small bulb even with the use of alcohol-carbon dioxide mixture, owing apparently to the presence of non-condensible gas. Therefore, a one-liter exhausted globe was inserted between two special joints, and, the bulb containing the tetrachloride having been warmed and the globe chilled with salt and ice, connection was made between the two and the globe was sealed off. Before the seal could be made several cubic centimeters of the tetrachloride distilled into the globe, carrying with it the bulk of the troublesome gas. This most volatile fraction, 1 (Figure 3), was hydrolyzed and the solid hydrolytic product when tested spectroscopically, except for a trace of arsenic seemed to contain nothing but germanium.

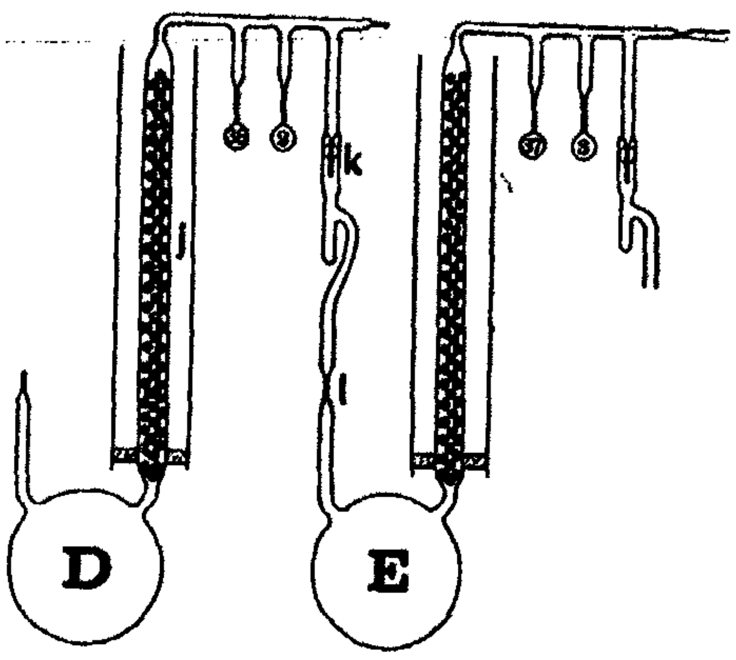

FIG. 2

In all twenty fractional distillations with Hempel columns were carried out in apparatus of the general type shown in Figure 2. The tetrachloride being in the exhausted bulb D and the fractionating column *j* being chilled with ice and water, a less volatile fraction was condensed in the small bulb 2 by means of alcohol and carbon dioxide and was sealed off at the capillary. The special joint *k* was then broken and the main bulk of the liquid was condensed in E with great care to have the fractionating column operating with greatest efficiency. When the residue in the still had been reduced to a few cubic centimeters the capillary *l* was sealed. The residue in D was finally condensed in bulb 38 by chilling with alcohol-carbon dioxide, the rest of the apparatus being warmed at the same time.

Purity of Germanium Tetrachloride

In this way all the tetrachloride was separated into fractions without accident, so that the material was not exposed to the air at any time after the introduction into the distilling apparatus. This fractional distillation is shown diagrammatically in Figure 3, in which the fractions are numbered in the order of decreasing volatility. The light and heavy fractions from the early distillations were tested for impurities as follows. The least volatile fractions from the first seven distillations were hydrolyzed with a considerable amount of water and treated with hydrogen sulfide. These showed rapidly diminishing proportions of arsenic. In fact, Fraction 34 seemed to be practically free from this impurity. The heavy residue from the eighth distillation, Fraction 33, was hydrolyzed with ammonia and the solution evaporated to dryness. This residue was tested spectrographically as described above and no evidence whatever of the presence of arsenic, tin or antimony could be detected. Dennis and Johnson[1] were able to detect 0.0005 per cent of arsenic in germanium by photographing the arc spectrum. We have no reason to believe that our spectroscopic procedure was any less sensitive.

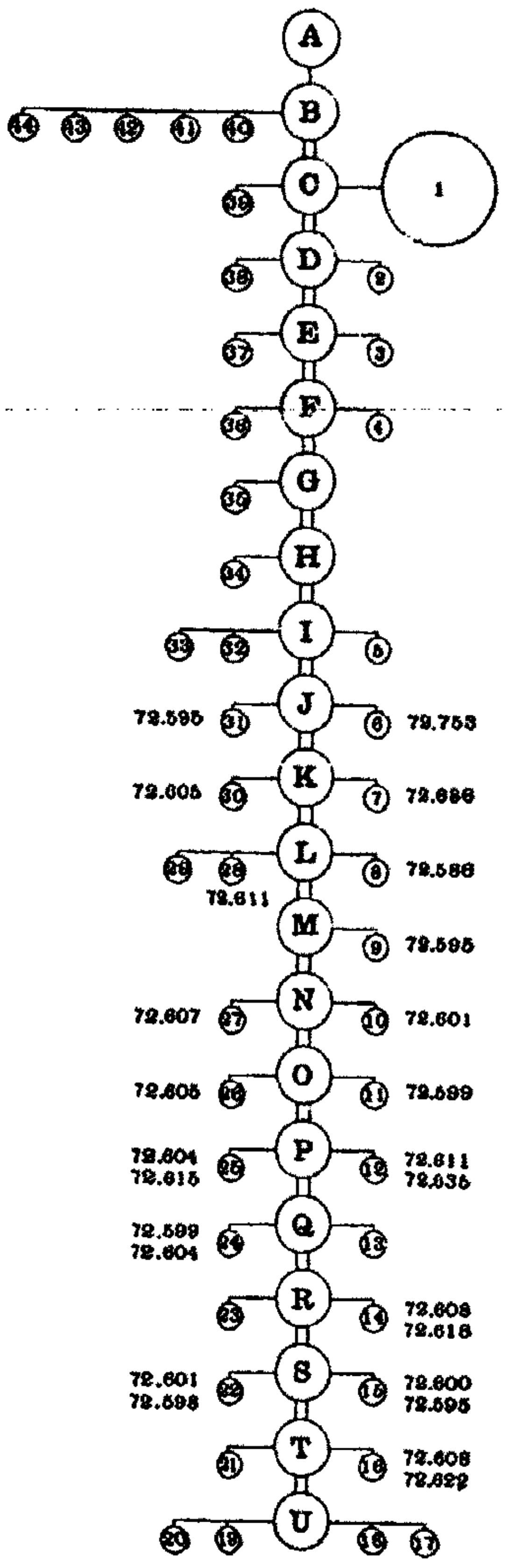

Fig. 3

Although in our experiments seven distillations were thus required for removing arsenic there is no question that, if a somewhat larger residue had been rejected in each distillation, fewer steps would have been necessary. Our somewhat limited quantity of material led us to proceed in a more cautious fashion. Although we have assumed that the arsenic was completely removed at this point, the residue of the eleventh distillation, Fraction 29, as well as Fractions 18 and 19 was tested spectrographically. No impurities of any sort could be detected.

Since the germanium tetrachloride was synthesized in a glass tube the possibility of the formation and presence of silicon tetrachloride existed. The boiling point of this substance, 58°, is so far below that of the germanium compound that rapid separation, but in the more volatile fractions, might reasonably be expected. Only one test for silicon was made. The contents of the

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[1] J. Am. Chem. Soc., 45, 1380 (1923).

bulb containing the most volatile fraction from the sixteenth distillation, Fraction 13, were added to a small amount of water in a clean platinum crucible and the crucible was nearly filled with constant boiling hydrochloric acid which had been distilled through a quartz condenser. Evaporation on an electric hot plate followed. Twice more in succession the crucible was filled with constant boiling hydrochloric acid and this acid was eliminated by evaporation. During these three evaporations the germanium was vaporized as chloride, while any silicon tetrachloride must have been hydrolyzed to silicic acid. The crucible was next ignited and carefully weighed by substitution. There was no evidence of any residue in the crucible except a small amount of platinum which had been dissolved by the acid. In order to expel any silica the crucible was next filled with hydrofluoric acid which had been freshly distilled through a platinum condenser, and after evaporation of the acid and ignition, the crucible was reweighed. The observed loss in weight 0.03 mg., is insignificant, and is as likely to be due to experimental error as to the presence of silicon tetrachloride. Even if this really represents silica impurity in the germanium tetrachloride, the corresponding amount of silicon tetrachloride, 0.09 mg., in a fraction weighing approximately five grams would lower the apparent atomic weight of germanium by only 0.001 unit.

The Analysis of Germanium Tetrachloride

The analysis of germanium tetrachloride followed closely the procedure used in the analysis of silicon tetrachloride.[1] After being weighed the bulb containing germanium tetrachloride was broken under an excess of sodium hydroxide and the glass was collected and weighed. The solution was diluted to considerable volume and made acid with nitric acid, and then was precipitated with a solution of a weighed, very nearly equivalent amount of pure silver. The point of exact equivalence between chloride and silver was then found with the assistance of a nephelometer. In several experiments the silver chloride was collected and weighed.

The bulb containing the material for analysis was first scrubbed with soap solution and then was allowed to stand for some time in sulfuric acid—dichromate solution. After thorough rinsing it was soaked for at least twenty-four hours in the purest water. From this point the bulb was not touched with the fingers. Next the bulb was placed in a basket of platinum wire which had already been weighed under water with an accuracy of one milligram, and the bulb and basket together were weighed under water of known temperature. Rinsing with pure water and draining were followed by drying, first over sulfuric acid, finally over potassium hydroxide which had been fused with permanganate to destroy organic matter. The bulb was then weighed by substitution and the density of the air in the balance case at the time of weighing was found by weighing a sealed standardized glass globe.[2]

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[1] Baxter, Weatherill and Scripture: Proc. Am. Acad., **58**, 245 (1923).

[2] Baxter: J. Am. Chem. Soc., **43**, 1317 (1921).

In order to hydrolyze the germanium tetrachloride without forming a semipermanent precipitate of germanium hydroxide, it was found advisable to dissolve the liquid in a solution of at least one hundred per cent excess of the sodium hydroxide necessary to form sodium chloride and sodium germanate. Furthermore, if the solution of sodium hydroxide was less concentrated than 4 normal at the time the reaction occurred germanium hydroxide was precipitated, although subsequent dilution of the solution did not result in precipitation.

A 4 normal solution of the sodium hydroxide was prepared in a heavy walled, two-liter Erlenmeyer Pyrex flask provided with a carefully ground glass stopper, the weight of glass in the bulb containing the tetrachloride being estimated in computing the amount of sodium hydroxide necessary. In the later analyses the sodium hydroxide solution was first filtered through a platinum sponge crucible. The weighed bulb was carefully introduced, and, before the stopper was inserted the flask was warmed gently so that ultimately the pressure should be slightly inward. After cooling the flask with tap water the inner walls of the flask were wetted with sodium hydroxide solution by inclining the flask and rotating, and then the bulb was broken by shaking the flask. A dense fog immediately appeared in the flask. Again the flask was cooled and although the fog disappeared in the course of fifteen minutes the flask was allowed to stand for three hours longer. In the first analysis a 2.5 normal solution of only fifty per cent excess of sodium hydroxide was used in the initial decomposition of the tetrachloride, and the precipitated germanium hydroxide could be dissolved only by long standing after adding more sodium hydroxide. In the third analysis the capillary of the bulb was first broken off and the precipitate which was formed by slow hydrolysis through the opening could be only imperfectly dissolved even by adding a large additional quantity of sodium hydroxide and long standing. In the sixth analysis although one hundred per cent excess of sodium hydroxide was used, the solution was only 2.5 normal when the bulb was broken. In this experiment also germanium hydroxide was precipitated and the precipitate could be ultimately dissolved only by the addition of more sodium hydroxide. In all the other analyses no difficulties of this sort were experienced.

The fragments of the glass bulb were collected on a weighed, platinum-sponge crucible. The solution was filtered directly into the glass-stoppered precipitating bottle or Erlenmeyer flask, and the glass was washed by decantation ten or twelve times with about one hundred cubic centimeters of boiling hot water and once with cold water before being transferred to the crucible. Drying at 300° for eighteen hours in an electrically heated porcelain air bath preceded the weighing of the crucible both empty and with the glass. In order to make sure that no germanium hydroxide was retained by the crucible and glass, the two were further treated with hot 4 normal nitric acid by slowly pouring from 400 to 800 cc. through the crucible. This treatment usually produced a slight loss in weight of a few hundredths of a milligram, but a second similar treatment produced no further change of appreciable magnitude.

Since it seemed likely, that during the treatment of the glass with sodium hydroxide and with acid solution would occur to some extent, experiments were carried out to test this point. A solution was prepared by dissolving germanium tetrachloride in sodium hydroxide solution as in an analysis, and was filtered through platinum sponge. The glass fragments of several bulbs were weighed in a platinum sponge crucible and then were allowed to stand in the above solution for some time. The glass was collected in the crucible in which it had been initially weighed and then was washed thoroughly with hot water and finally with hot 4 normal nitric acid. Drying at 300° followed. After being weighed a second time the glass was washed with hot nitric acid, dried and weighed until the weight was constant. In the first four experiments the glass consisted of a mixture of fragments of different sizes and shapes. In Experiment 5 coarse fragments, in Experiment 6 fine fragments were used. The weights given in the table represent differences between the crucibles and counterpoises.

The slight gain in Experiment 2 is apparently due to an undetected accident. In the other five experiments the losses are consistent with the conditions and indicate an average loss in weight of 0.007 mg. per gram of glass per hour of treatment with the alkaline germanate solution, combined with the nitric acid treatment. A correction of this magnitude was therefore applied to the weight of glass obtained in each analysis. Except in Analyses 1, 3 and 6 (Table IV) this correction did not exceed 0.03 mg.

From the observations with the bulb before breaking and the weight of glass corrected as above and for the buoyant effect of the air, the weight of germanium tetrachloride was found. The weight of silver necessary to precipitate the chloride was computed, and was weighed out, chiefly in the form of a very few large buttons, the final adjustment being made with small electrolytic crystals. After careful solution of the silver in chloride-free nitric acid and elimination of nitrous acid by heating the solution, in a flask provided with a spray trap in the form of a column of bulbs ground into the neck of the flask, fifty cubic centimeters additional of concentrated nitric acid were added, together with sufficient water to make the solution nearly normal in silver. The acid solution was then added slowly with continual agitation to the germanium solution which had been diluted to less than normal concentration during the washing of the glass and also had been made acid by adding 4 normal nitric acid through a funnel tube extending to the bottom of the solution. The mixture was allowed to stand for several days with occasional shaking, and the solution was tested for excess of chloride or silver in a nephelometer. If an excess of either was found, the deficiency of the other was made up by adding hundredth normal silver nitrate or potassium chloride until the endpoint had been reached. In the earlier analyses it was necessary to add a considerable amount of chloride in this way because the atomic weight of germanium assumed at the beginning was considerably lower than that actual-

TABLE II

Solution of Glass by Alkaline Sodium Germanate

Experiment	Wt. of glass gm.	Crucible + glass before treatment with alkali gm.	After treatment with alkali gm.	After treatment with HNO_3 gm.	After treatment with HNO_3 gm.	Glass dissolved gm.	Period of treatment with alkali hours	Glass dissolved per hour per gram
1	2.212	0.25764	0.25659	0.25644	0.25648	0.00120	69	0.000008
2	3.888	0.52810	0.52844	0.52827	0.52826		5	
3	2.212	0.25648	0.25639	0.25637		0.00011	7	0.000007
4	2.206	0.82372	0.82344	0.82350		0.00028	16	0.000008
5	3.616	4.61864	4.61836	4.61834		0.00030	20	0.000004
6	3.839	4.13618	4.13588	4.13585		0.00033	6	0.000010

ly found. In the later analyses the correction to produce equivalence amounted to only a few tenths of a milligram of silver. Even after the apparent endpoint had been reached the solutions were allowed to stand for some weeks longer with occasional shaking in order to allow included or occluded material to be extracted from the precipitate of silver chloride. Although at the beginning of a comparison of this sort the endpoint is likely to alter somewhat with time after two or three weeks have elapsed only slight changes are likely to be produced.

The manipulations of precipitation and testing of the solutions were always carried out in ruby light. In using the nephelometer all the precautions noted by Richards and Wells[1] were observed, such as preparing the comparison tubes under as nearly as possible identical conditions of temperature, concentration and time, allowing the tubes to come to constant ratio by standing for an hour or more, and taking the average of several readings of each ratio.

In the last seven analyses the silver chloride was collected on a platinum sponge crucible and weighed. First the solubility of the silver chloride was reduced by adding an excess of silver nitrate and cooling to 0° for twenty hours with occasional shaking. In Analyses 19-22 one-half gram of silver nitrate was added, in Analyses 23-25 one gram. This relatively large excess of silver nitrate seemed advisable because of the comparatively large amount of nitric acid and sodium nitrate in the solution which increase the solubility of the silver chloride materially. Filtration of the supernatant liquid through a large weighed platinum sponge crucible was followed by thorough washing of the precipitate by decantation with a chilled solution of silver nitrate containing 0.05 gram per liter. The precipitate was transferred to the crucible with chilled water, and after being dried in an electrically heated porcelain oven for about eighteen hours at 300° it was weighed. Moisture retained by the precipitate was determined by fusing the main bulk and finding the loss in weight. In the first two experiments, Analyses 19 and 20, faulty technique may have occasioned too large a loss in weight. The later experiments show a water content of the precipitate more nearly in accord with other experiments of the same sort.

No correction is applied for silver chloride dissolved in the mother liquor. The solubility of silver chloride in the chilled silver nitrate washings was assumed to be 0.03 mg. per liter. This correction was never larger than 0.05 mg. The precipitating flask was rinsed with ammonia and the rinsings were added to the aqueous washings. The resulting solution was diluted to a

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[1] Richards: Am. Chem. J., 31, 235 (1904); 35, 510 (1906)

definite volume, either 500 cc. or 1000 cc., and its chloride content was found by comparison with standard chloride solutions in a nephelometer after adding nitric acid and silver nitrate.

In the tables the original weight of silver chloride has been corrected for chloride introduced in the comparison of the germanium chloride with silver. The results of all the analyses undertaken are given.

Weighings were made on a No. 10 Troemner balance, sensitive to 0.02 mg. with a load of fifty grams. A 5 milligram rider was used to determine quantities less than this and more than 0.05 mg. Interpolation from zero points was employed only for amounts less than 0.05 mg.

The weights were of gold plated brass, except the fractional weights which were of platinum, and were compared by the Richards substitution method.[1]

All weighings were by substitution. In the case of the bulb and silver, the weights were substituted for the object weighed. In the case of the glass and the silver chloride the crucibles were substituted for similar counterpoises. A small quantity of impure radium bromide was kept in the balance case to prevent electrostatic effects.

Vacuum corrections were applied as follows:

TABLE III

Vacuum Corrections

	Density	Vacuum correction per gram
Weights	8.3	
Air	0.001293 at 0° and 760 mm.	
Glass	2.5	+0.000335
Silver	10.49	−0.000031
Silver chloride	5.56	+0.000071

Discussion of Results

In the following table the results are arranged in the order of decreasing volatility of the fractions analyzed.

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[1] Richards: Jour. Chem. Soc., **22**, 144, (1900).

Results

TABLE IV

The Atomic Weight of Germanium

Ag = 107.880 GeCl$_4$:4 Ag Cl = 35.458

Number of analysis	Fraction of GeCl$_4$	Weight of GeCl$_4$ in vacuum gm.	Weight of Ag in vacuum gm.	Weight of Ag added or subtracted in solution gm.	Corrected weight of Ag in vacuum gm.	Ratio GeCl$_4$: 4 Ag	Atomic weight of germanium
1	6	4.32030	8.69804	−0.01010	8.68794	(0.497276)	(72.753)
2	31	4.86658	9.80158	−0.00790	9.79368	0.496910	72.595
3	7	5.16272	10.38923	−0.00400	10.38523	(0.497121)	(72.686)
4	30	3.85268	7.75236	+0.00055	7.75291	0.496933	72.605
5	8	4.67090	9.39916	+0.00110	9.40026	0.496891	72.586
6	28	4.27610	8.60360	+0.00110	8.60470	0.496949	72.611
7	9	5.96671	12.00707	+0.00050	12.00757	0.496912	72.595
8	10	4.53734	9.13063	+0.00020	9.13083	0.496925	72.601
9	27	3.11571	6.26925	+0.00055	6.26980	0.496939	72.607
10	11	3.97498	7.99912	+0.00010	7.99922	0.496921	72.599
11	26	5.07110	10.20445	+0.00030	10.20475	0.496935	72.605
12	12	4.91397	9.88796	+0.00035	9.88831	0.496947	72.611
13	25	6.05244	12.17973	−0.00010	12.17963	0.496931	72.604
14	24	5.21384	10.49237	−0.00005	10.49232	0.496920	72.599
15	14	5.20164	10.46750	−0.00020	10.46730	0.496942	72.608
16	15	4.34510	8.74401	0.00000	8.74401	0.496923	72.600
17	22	4.18788	8.42750	+0.00010	8.42760	0.496924	72.601
18	16	4.24281	9.53775	+0.00010	8.53785	0.496941	72.608
			Average omitting Analyses 1 and 3			0.496928	72.602

TABLE V

$GeCl_4:4\ AgCl$

Number of analysis	Fraction of $GeCl_4$	Weight of $GeCl_4$ in vacuum gm.	Weight of AgCl in vacuum gm.	Loss on fusion gm.	Dissolved AgCl gm.	Corrected weight of AgCl in vacuum gm.	Ratio $GeCl_4$: 4 AgCl	Atomic Weight of germanium
19	12	4.91397	13.13679	0.00054	0.00068	13.13693	0.374058	72.635
20	25	6.05244	16.18131	0.00059	0.00130	16.18202	0.374024	72.615
21	24	5.21384	13.94013	0.00019	0.00066	13.94060	0.374004	72.604
22	14	5.20164	13.90641	0.00021	0.00090	13.90710	0.374028	72.618
23	15	4.34510	11.61745	0.00016	0.00097	11.61826	0.373989	72.595
24	22	4.18788	11.19722	0.00013	0.00064	11.19773	0.373994	72.598
25	16	4.24281	11.34233	0.00016	0.00114	11.34331	0.374036	72.622
					Average		0.374019	72.612
					Average, omitting Analyses 19 and 20		0.374010	72.607
					Average of all analyses except Analyses 1, 3, 19 and 20			72.603

TABLE VI

Atomic Weight of Germanium

Fraction	Atomic weight $GeCl_4:4\ Ag$	Atomic weight $GeCl_4:4\ AgCl$
6	72.753	
7	72.686	
8	72.586	
9	72.595	
10	72.601	
11	72.599	
12	72.611	72.635
14	72.608	72.618
15	72.600	72.595
16	72.608	72.622
22	72.601	72.598
24	72.599	72.604
25	72.604	72.615
26	72.605	
27	72.607	
28	72.611	
30	72.605	
31	72.595	

Aside from the first two fractions, no systematic trend is apparent, and in view of the uniformity of the material over a wide range of fractions, the conclusion may reasonably be drawn that the purification of the germanium tetrachloride had been carried as far as it is possible to carry it by the method of fractional distillation. Furthermore, direct evidence of the absence of arsenic and silicon in the fractions analyzed was secured. So far as hydrogen chloride is concerned, the uniformity of the material is the only evidence which can be adduced that this substance had been eliminated. However, aside from the possibility of the existence of a constant boiling distillate of germanium tetrachloride and hydrogen chloride, the wide difference in boiling points of the two substances would lead to the expectation of rapid separation at the start.

The high results of the analyses of Fractions 6 and 7 cannot be ascribed to the presence of arsenic since these fractions were the *most* volatile of those analyzed. These two analyses were the first and third undertaken and as explained on page 1057 considerable difficulty was experienced in the hydrolysis of these fractions. Since it seems unlikely in view of the uniformity of the rest of the material that these fractions were really different from the rest, the more complicated and protracted manipulation and technical inexperience with the method seem to us more probable reasons for the divergence.

Aston[1] has recently found by means of the mass spectrograph that germanium consists of at least three isotopes of masses 74, 72, and 70, the relative

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[1] Aston: Nature, 111, 771 (1923).

abundance being that of the order listed. He also states that the atomic weight 72.5 is not incompatible with the apparent proportions of the three isotopes. A difference in observed atomic weight of 0.1 unit is not likely to introduce inconsistency in this situation. With two isotopes of chlorine, there are evidently possible fifteen tetrachlorides of germanium with molecular weights ranging, with intervals of two units, from 210 to 222. The unlikelihood of appreciable separation of such isotopic molecules during fractional distillation has already been emphasized in the case of silicon and boron halides. Furthermore, as pointed out in the case of the boron halides, experimental evidence that isotopic separation is inappreciable is furnished by the ratios between the silver used in a comparison with the germanium chloride and the silver chloride obtained in the second step in the same analysis, since separation of the chlorine isotopes is as probable as that of the germanium isotopes. In the following table these ratios are given.

TABLE VII

Analyses	Fraction of $GeCl_4$	Ratio Ag: AgCl
12 and 19	12	0.752711
15 22	14	0.752659
16 23	15	0.752609
18 25	16	0.752677
17 24	22	0.752617
14 21	24	0.752645
13 20	25	0.752664
	Average	0.752655
Average, excluding Fractions 12 and 14		0.752642
Richards and Wells found		0.752627

As explained on page 1060 the silver chloride determinations in Analyses 19 and 20 are subject to some uncertainty in the estimation of the moisture. Furthermore it is certain that silver chloride cannot be made wholly insoluble by the addition of silver nitrate in excess. In fact we found that by adding more silver nitrate to the filtrate of Analysis 22 a very slight but unmistakable opalescence was produced. Winkler[1] found that silver chloride precipitated in the presence of germanium carried down germanium hydroxide. Although the results of our chloride determinations show little indication of such an effect, the silver chloride from Analyses 24 and 25 was tested for germanium spectrographically on graphite electrodes. In both cases a trace of germanium was present, for the line λ 2651 was faintly visible in both cases, although the two lines λ 3039 and λ 3270 could not be seen in the photographs. From previous experience with other elements we estimate the proportion of germanium in the silver chloride as less than 0.001 per cent. This proportion would affect the atomic weight of germanium by 0.002 unit.

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[1] J. prakt. Chem., (2) 34, 177 (1886).

There is no reason to believe that this slight contamination of the silver chloride is unique in the case of germanium. It is a question whether it is possible by a single precipitation to prepare absolutely pure silver chloride, owing to the phenomena of inclusion and occlusion. Furthermore, experience in the past has been that in this type of analysis the results of a comparison with silver is in general slightly higher than that of a silver halide determination, a fact which is in accord with the idea that slight contamination of the silver halide invariably occurs.

Because of these two uncertainties, solubility and contamination, a silver chloride determination is sure to be somewhat less reliable than a comparison with silver.

It is difficult to reconcile the result of this investigation with that of Müller, 72.418. From the standpoint of simplicity in the formula of the substance analyzed, however, much can be said in favor of the tetrachloride over the potassium fluorgermanate. Further investigation is obviously necessary and we propose to prepare and analyze the tetrabromide of germanium as the next step.

Summary

1. A method for the purification of germanium tetrachloride from arsenic trichloride by fractional distillation in exhausted vessels is described.

2. The atomic weight of germanium has been found to be 72.60 by analysis of germanium tetrachloride.

We are especially indebted to the Bache Fund of the National Academy of Sciences for generous assistance in providing much of the necessary apparatus and materials, and to the New Jersey Zinc Company for the gift of the germaniferous zinc oxide.

Cambridge, Mass.

THE CATALYTIC ALKYLATION OF AMMONIA[1]

BY A. B. BROWN AND E. EMMET REID

Introduction

Sabatier and Mailhe[2] have shown that a mixture of primary, secondary and tertiary amines is formed by passing the vapor of an alcohol with ammonia over a variety of catalysts at elevated temperatures. Alumina, titania, zirconia, chromic oxide, the blue oxide of molybdenum, thoria, and the blue oxide of tungsten have been listed as catalysts, the last two mentioned being commonly regarded as the most efficient. While considerable qualitative data are available, the theoretical and practical importance of the reaction makes it advisable to secure more quantitative information than is now at hand. Hence the present investigation has for its purpose the quantitative study of the alkylation of ammonia by methyl, ethyl, n-propyl, and n-butyl alcohols, using various catalytic oxides at temperatures up to 500°C.

On account of the favorable reports that have been made of the activity of the blue oxide of tungsten in this reaction, much time was spent on it, the catalyst being prepared in a number of different ways in the hope of finding an active preparation but the yields of amines with it were all poor.

Thoria gave good yields of amines but also much aldehyde, the most of which passes into the nitrile.

Silica gel proved to be comparable to freshly prepared thoria in percentage conversion and much superior to thoria as well as alumina and zirconia in length of catalytic life and in freedom from destructive action on the alcohol not aminated. The peculiar thing about silica gel is the wide variation in its activity with seemingly slight variations in its preparation. A single sample of silica gel will give reproducible results, but two lots prepared in apparently the same way show different activity. A slow setting (6 to 9 hours) gel made from c.p. chemicals in exact proportions, thoroughly washed and slowly dried is apt to be an active catalyst. Silica gel impregnated with nickel oxide gave poor results; impregnated with thoria, fairly good. Commercial silica gel is a very poor catalyst for this reaction though in esterification it is almost as good as the specially prepared.[3]

Apparatus

The furnace used was the same as described by Kramer and Reid[4] and the methods of operation similar. The anhydrous alcohol, accurately measured from a regulated dropper and calibrated tip, passed through a vertical tube

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[1] From dissertation of A. B. Brown, du Pont Fellow.

[2] Sabatier: Catalysis in Organic Chemistry, translated by Reid, p. 263, (1922); Sabatier and Mailhe: Compt. rend., 143, 1204 (1901); 148, 898 (1909); 150, 823 (1910); 153, 160 (1911).

[3] Milligan and Reid: unpublished results.

[4] J. Am. Chem. Soc. 43, 880 (1921).

to the bottom of a 150 c.c. distilling bulb, immersed in an oil bath kept at 250°-300°, which served as a vaporizing and mixing chamber and preheater. Ammonia, from a cylinder, passed through a calibrated flowmeter and entered the mixing chamber through a side tube sealed into the vertical alcohol inlet tube. The reactants, passing from the side arm of the vaporization bulb, were led through an extension of the catalytic tube, where they were brought to the proper temperature by an electric preheating coil, and thence over the catalyst in the reaction tube, a pyrex tube (1.5-2 cm.×45 cm.) uniformly heated in a horizontal electric furnace automatically regulated to within 1°, as read on a thermocouple laid beside the catalyst tube. The products of the reaction passed from the catalytic tube through a condenser into a collection bottle. A threeway stop-cock interposed permitted samples of the condensate to be taken without disconnecting the main receiver.

Analysis

After an extensive study of all the methods[1] that have been proposed for such mixtures we decided on the following plan, which is essentially that proposed by Weber and Wilson[2], though we did not come across their work until after our own was done. The method was tested out on known mixtures and the corrections thus found applied to the unknowns.

The reaction products were run for the desired time into standard sulphuric acid and titrated back with methyl red as indicator to determine total basic nitrogen. The solution was divided into aliquots, in one of which the total amine nitrogen was found by the method of François[3] based on the selective precipitation of ammonia in presence of amines in a sodium hydroxide—carbonate solution by yellow mercuric oxide. The difference of these two represents the ammonia. In a second ammonia and primary amine are determined together by the method of van Slyke[4] for the estimation of the amino group, the decomposition being effected at 90°. Tests with pure ammonium chloride and the hydrochloride of butyl amine prepared by the reduction of nitrobutane gave results 2% high—agreeing with van Slyke's observations on other amino compounds. Subtracting the previously determined ammonia from the van Slyke values gives the primary amine.

To estimate tertiary amine a third aliquot is placed in a 200 c.c. flask and sufficient sodium nitrite added to make a 25% solution. This is heated for an hour under reflux on a water bath, acetic acid being added from time to time to maintain slight acidity. A trap containing dilute sulphuric acid is connected with the top of the condenser to guard against loss of amine. After cooling the solution is transferred to a Kjeldahl still, nitrogen oxides blown

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[1] Heintz: Ann. **127**, 43 (1863); Hofmann: Ber. **3**, 776 (1870); Hinsberg: **23**, 2962 (1890); **33**, 3526-9 (1900); Hinsberg and Kessler: **38**, 906 (1905); Sudborough: Proc. Roy. Soc., **20**, 165 (1904); J. Chem. Soc., **95**, 447 (1909); Bertheanme: Compt. rend., **150**, 1251-3 (1901); **151**, 146-9 (1911).

[2] J. Biol. Chem. **35**, 385 (1918).

[3] J. pharm. chim. (6) **25**, 517 (1907); Compt. rend. **144**, 567-9 (1907) 857-9 (1907).

[4] Ber. **43**, 3170 (1910).

off and strong alkali added, after which the tertiary amine is distilled into standard sulphuric acid and back titrated with methyl red as indicator. The secondary amine is estimated by difference from the above determinations.

The estimation of nitrile is effected by hydrolysis of an aliquot of the sample with 48% sulphuric acid in a pressure bottle at 100° for 1 hour. The product is diluted and steam distilled into 0.1 N. alkali and back titrated using phenolphthalein to determine the acid resulting from the hydrolysis of the nitrile.

Inasmuch as the amines are estimated through their nitrogen value, a complete analysis of a sample for primary, secondary, and tertiary amines is necessary for the determination of the percentage of alcohol converted into amines, since primary, secondary, and tertiary amines are equivalent as regards ammonia but stand in the ratios of 1:2:3 as to the alkyls used up. Consequently, two values for percentage alkylation will be met with in the following tables of experimental results: the one, used when only amine was estimated, termed simply "% amines" which gives the number of molecules of amines from 100 of alcohol, the other "% alkylation", used when complete analyses were made for promary, secondary, and tertiary amines. This value represents the amount of alcohol converted into amines. On the average this figure is 1.69 times the percent of amines, varying, of course, with the ratio of secondary and tertiary to primary, but remaining quite constant for butyl alcohol. In cases where complete analyses were not made, the percent of alcohol aminated can be approximated by multiplying the molecular percent by this factor. For the preliminary comparison of catalysts and for finding the optimum temperatures with various catalysts it is sufficient to consider the total amines formed as set down under "% amines".

Analysis of the gases was effected by collection of a timed sample in a Hempel burette over dilute sulphuric acid, adsorption of the ethylene hydrocarbon by fuming sulphuric acid, and determination of the residual hydrogen by explosion. The gas left after shaking with fuming sulphuric acid was always found to contain practically nothing but hydrogen.

A nitrile may be formed either from an aldehyde or from a primary amine with the liberation of 4 atoms hydrogen. We know little of the speed of the dehydrogenation of the primary amine but as relatively little of it is present during the passage of the mixture over the catalyst, it has been assumed, as a rough approximation, that all the nitrile was derived from the aldehyde, the amount of which can thus be calculated from the hydrogen found.

Experimental

Thoria Catalyst

In view of the efficiency of thoria as a dehydrating catalyst, this was the first catalytic substance employed. Catalyst A was prepared by pouring over enough shredded asbestos to fill the catalytic tube an almost saturated solution of thorium nitrate corresponding to 25 g. thoria, and evaporating to dryness in a vacuum desiccator over sulphuric acid. The resulting hard mass was shredded into small fragments, packed in the catalytic tube, and heated to

TABLE I—*Catalyst A*

Butyl Alcohol and Ammonia over Thoria—Asbestos.

Run	I	II	III	IV	V	VI		I		
NH_3/BuOH	1.5	2.4	1.6	1.15	1.5	1.5		1.5		
Rate	6	9	3.1	8.9	6	6		6		
Hrs. previous use of catalyst	0	10	15	20	30	40		0		
Temp.		Percent	Amines	Formed.			prim.	sec.	tert.	% Alkylation
360°	——	16.7	7.0	10.2	4.0	——	——	——	——	——
370°	25.3	——	7.6	12.7	3.6	——	15.9	3.9	5.5	40.2
380°	27.3	19.3	——	——	——	——	13.1	7.4	6.8	48.3
390°	28.0	21.3	8.1	14.6	5.1	8.9	14.6	8.9	4.5	46.0
410°	22.6	——	7.2	17.2	5.9	——	8.9	9.7	4.0	40.3
420°	——	16.8	——	12.9	6.3	——	——	——	——	——
430°	15.4	16.3	7.4	——	——	——	8.6	2.2	4.6	26.9

270°-300° in the furnace whereby the nitrate was converted to the oxide. After complete conversion, the catalyst was thoroughly scrubbed out with moist air at 400°C.

This catalyst was employed for the amination of butyl alcohol as shown in Table I. Some of the runs were at temperatures differing slightly from those given, but, as the temperature coefficient is not great, they have been grouped. The rate is time in hours required for the passage of one mole of the catalyst. For only the first run were the amines determined separately. The figures for these are given in the right hand portion of the table, together with the percent of alkylation.

The optimum temperature is 380°-390° for a fresh catalyst but rises to 420° or higher with prolonged use, the deterioration of the catalyst being more rapid during the first part of its life period. After having become coated with a carbonaceous deposit, the catalyst may be regenerated by treatment for several hours with moist oxides of nitrogen at 380°-400° followed by moist air, but does not recover its original activity, as is shown by run VI above. The regenerated catalyst is pure white but its surface is distinctly different—appearing grainy rather than powdery as it did originally.

Catalyst B likewise containing 25 g. thoria, was made in a similar manner with pumice as carrier.

This catalyst was tested with butyl alcohol at the rate of 1 mole in 5.8 hours with 1.3 equivalents of ammonia, with the following results:

TABLE II

Temp.	326°	342°	355°	369°	385°	396°
% Amines	1.64	3.65	4.18	6.65	8.55	10.2

The catalyst became darkened by a slight deposit but still appeared to be in good physical condition with a characteristic smooth surface.

Gas Evolution

Thoria has been rated by Sabatier[1] as a dehydration catalyst exclusively but Kramer and Reid[2] found only 2.7% of butylene to 32.7% of butyric aldehyde produced by their thoria catalyst at 380°, from which it appears that different preparations of thoria give widely different results. When ammonia is present the aldehyde formed is largely, but not completely converted, into nitrile with the evolution of a second molecule of hydrogen. Actually the furnace product gave, on distillation, a small fraction which smelled of aldehyde and gave the aldehyde test with fuchsine solution.

A run was made using the thoria-asbestos catalyst A with butyl alcohol vapor, 1 mole in 5.6 hours, and a slight excess of ammonia, the gas being collected and analyzed. If all of the alcohol had been converted to aldehyde 64.3 c.c. of hydrogen should have been formed per minute, if into nitrile, 128

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[1] Sabatier: "Catalysis in Organic Chemistry." 233, (1922).

[2] J. Am. Chem. Soc. 43, 884 (1921).

c.c. and if into butylene, 64.3 c.c. of C_4H_5. The results are given in Table III, the volumes given being cubic centimeters obtained per minute reduced to 0° and 760 mm.

TABLE III

Gases evolved from Butyl Alcohol and Ammonia

Temp.	Total Gas	C_4H_6	H_2	% Alcohol converted into C_4H_8	Nitrile
360°	10.3	1.17	8.97	1.82	7.04
374°	16.02	2.26	13.34	3.52	10.41
390°	29.87	4.02	23.90	6.25	18.6
405°	33.21	4.17	29.05	6.48	22.6
420°	57.28	8.04	49.25	12.5	38.3

The figures under "nitrile" were calculated on the assumption that all of the aldehyde formed had been converted into nitrile, that is by dividing the percentage of hydrogen by 2 which over-estimates the nitrile since some of the aldehyde remained as such. In a similar run using 1.45 mol. of ammonia to 1 of alcohol at the same rate, the nitrile was found to be 11.05 and 22.3% at 380° and 410° whereas calculated as above it would have been 12.8 and 29.5% Calculating the aldehyde from the hydrogen remaining after subtracting that corresponding to the nitrile we have 3.5 and 14.4% of aldehyde remaining as such. Our thoria-asbestos was a poor catalyst for dehydrating butyl alcohol but excellent for producing aldehyde and nitrile by dehydrogenation. Above 400° a large proportion of the alcohol is used up in side reactions.

Tungstic Oxide Catalysts

Catalyst C. A tungstic acid hydrate gel[1] was made by the gradual addition of 6.38 N. nitric acid to a 12% solution of sodium tungstate, slowly until the first formed precipitates redissolves, then rapidly with vigorous stirring until the colorless solution takes on a clear yellow green color, the total acid required being 2.5 to 3.0 times the sodium tungstate equivalent. The gel after having set is thoroughly washed, and slowly dried at gradually increasing temperatures, and finally reduced at 300° with hydrogen to the blue oxide. Two runs were made using 78 g. of the reduced blue oxide gel.

Catalyst D. Unhydrated tungstic acid prepared by precipitation with hot concentrated hydrochloric acid from a hot solution containing 25 g. sodium tungstate, was thoroughly washed made and in the form of a thin paste was distributed over small fragments of pumice. This material was then slowly dried and reduced at 275°-300° with ethyl alcohol vapor carried over it by air.

Catalyst E. Pumice in small fragments was impregnated with 25 g. tungstic acid dissolved in aqueous ethyl amine, dried, packed in the catalyst tube and heated to 300° in current of air. The trioxide was then reduced to

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[1] Method worked out in this laboratory by Dr. C. H. Milligan to whom we are indebted for 32 g. of this gel.

the blue with alcohol vapor at 350°. The resulting catalyst was notable for its adherent qualities and even distribution of the blue oxide.

Catalyst F was prepared by suspending 40 g. of commercial blue oxide of tungsten powder on pumice.

The efficiency of these catalysts in amination was found to be surprisingly low, the most active being that form ethyl amine tungstate. Though each of the blue oxide of tungsten catalysts were subjected to 10 to 12 working hours of catalysts, their physical properties seemed entirely unimpaired—no carbonization being observed. The best temperature and highest yields with these catalysts are given in table IV.

TABLE IV

Alcohol and Ammonia 1:1.5 over Oxide of Tungsten

Catalyst	C	C	D	E	F
Alcohol	Butyl	Butyl	Butyl	Butyl	Ethyl
Rate	8	5.7	5.2	5.2	5.8
Temp.	365°	365°	320°	365°	400°
% Amines	2.98	1.55	3.43	6.22	7.73

The gases evolved were collected and analyzed with catalyst E at 365° with the following results:

Temp.	Total gas	C_4H_8	H_2	%C_4H_8	% Nitrile
365°	23.3	19.4	3.9	26.8	2.69
365°	20.8	17.8	3.0	25.3	2.18

from which it appears that the blue oxide of tungsten is a decided dehydration catalyst—agreeing well with the findings of Sabatier and Mailhe[1].

Other Catalysts

Catalyst G consisted of 20 g. of alumina precipitated on pumice from sodium aluminate by sulphuric acid. It became heavily carbonized in a single run with butyl alcohol and ammonia.

Catalyst H was prepared similarly to B using 25 g. zirconium nitrate on pumice. It carbonized badly in a single run.

Catalyst I was 30 g. of a laboratory sample of silica gel which had been kept for about a year in contact with the air. After a run with butyl alcohol it was considerably discolored, amber to dark brown, but showed no surface deposits.

Catalyst J[2] was 30 g. of silica gel impregnated with a small percentage of thoria. It showed only slight discoloration in one run.

Catalyst K[2] was 30 g. of silica gel impregnated with nickel oxide which was reduced by the alcohol. It proved to be an active dehydrogenation catalyst producing much nitrile. It discolored about as I.

The performances of these catalysts can be seen in the following Table, V, which gives the optimum temperatures and percent of amines formed.

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[1] Ann. chim. phys. [8] 20, 328 (1910).

[2] For catalysts J and K we are indebted to Dr. E. H. Barclay of this laboratory.

TABLE V

Butyl Alcohol and Ammonia, 1:1.5

Catalyst	G	H	I	J	K
Rate	5.6	5.75	5.58	5.75	5.8
Temp.	380°	360°	390°	360°	350°
% Amines	6.55	15.0	4.60	16.4	9.63

At 350° and at 405° with catalyst K analysis showed 24.7 and 40.1% of nitrile on the alcohol used.

Silica Gel

Our gel was prepared[1] by adding, with vigorous stirring, a sodium silicate solution (4.5% Na_2O) to an equal volume of 10% pure hydrochloric acid. After the gel sets, it is broken into large fragments which are placed in a tray having a bottom of wire netting and suspended in running water for several days. The gel is dried at temperatures rising by stages to 180° before being placed in the catalyst tube.

For charging the reaction tube 30 g. of the gel in fragments 0.5 to 0.7 cm. were required. After running for 25 hours with butyl alcohol and ammonia there was no diminution in the activity of this catalyst. All of the runs in the following Table VI were made with the same sample[2] of catalyst, the runs are numbered in the order in which they were made.

TABLE VI

Alcohols with Ammonia 1:1.5, Special Silica Gel

Run	3	2	4	5	1
Alcohol	Methyl	Ethyl	Ethyl	Propyl	Butyl
Rate	5.9	5.6	5.6	6.2	5.5
Temp.	Percent		Amines	Formed	
300°	——	——	——	——	3.7
320°	5.4	5.1	5.6	14.6	5.4
340°	8.4	9.5	8.9	19.8	6.5
360°	12.4	12.7	12.1	24.1	8.1
380°	17.0	18.5	19.9	26.4	11.7
400°	23.3	25.6	25.6	29.6	18.3
420°	31.0	31.1	30.8	32.4	20.7
430°	——	——	——	——	20.4

Propyl alcohol appears to be the most readily aminated. About 400°-420° is the best temperature.

The run of butyl alcohol was continued for 3 hours using 0.56 mole of the alcohol. The lower layer of the product weighed 8.59 g. and contained 0.0034 moles of amines while the top layer weighed 24.78 g. with 0.11 moles of amines or 20.3%. A new run was made with the same gel and samples taken at intervals with the following results: after 1 h. 22.8%, after 6 h. 23.2%. After standing cold over night it was started again and gave: after 1 h. 22.4%, after 3 h. 20.7% and after 6 h. 22.9% amination.

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[1] Method in use in this laboratory due to Dr. Patrick.

[2] Kindness of Dr. E. H. Barclay of this laboratory.

The gases evolved were studied and found as follows:

TABLE VII

Temp.	Alcohol	Gas per min.	C_nH_{2n} c.c.	H_2 c.c.	C_nH_{2n} %	H_2 %
400	Ethyl	7.77	3.28	4.48	4.72	3.22
415	Butyl	8.90	6.75	2.15	10.90	1.75 (fresh gel)
415	Butyl	12.85	7.85	5.00	12.80	4.06 (long used gel)

From these figures it appears that silica gel dehydrates moderately well but dehydrogenates much less than thoria, which is a great advantage in this reaction.

More extensive runs and complete analyses on methyl, ethyl, n-propyl and n-butyl alcohols using fresh samples of gel in each case gave the results of Table VIII.

TABLE VIII

Alkylation of Ammonia by Various Alcohols over Silica Gel.

1 Mole Alcohol to 1.5 Ammonia in 6 hours.

Alcohol	Temp.	Percent Amines				% Alkylation
		Total	Prim.	Sec.	Tert.	
Methyl	328°	4.9	——	——	——	——
	360°	9.0	——	——	——	——
	395°	16.1	——	——	——	——
	423°	25.7	5.9	17.6	2.2	47.7
	447°	29.8	——	——	——	——
	481°	34.1	14.3	17.9	1.9	55.8
	510°	32.8	——	——	——	——
Ethyl	354°	4.9	——	——	——	——
	395°	10.6	——	——	——	——
	415°	15.5	4.3	7.4	3.8	30.6
	436°	19.2	——	——	——	——
	456°	21.5	7.8	9.7	4.1	39.4
	477°	22.2	——	——	——	——
	500°	17.3	——	——	——	——
	520°	14.2	——	——	——	——
Propyl	300°	8.0	——	——	——	——
	331°	12.7	——	——	——	——
	359°	18.7	7.6	10.3	0.76	30.6
	388°	27.8	——	——	——	——
	420°	32.9	19.5	10.8	2.6	48.8
	448°	19.5	15.1	3.0	1.4	25.4
	468°	9.0	——	——	——	——
	490°	3.1	——	——	——	——
Butyl	381°	10.5	0.45	9.6	0.53	21.4
	407°	15.3	7.4	7.1	0.81	24.0
	430°	17.4	10.9	5.4	1.14	25.0
	472°	12.7	8.4	2.9	1.45	18.6

A different preparation of gel showed with butyl alcohol a similar maximum yield but a sharper break in the temperature-yield curve, under similar conditions, as Table IX indicates.

Table IX

System BuOH-NH_3

Temp.	320°	354°	381°	396°	420°	452°	472°	493°
% Amines	3.29	4.77	9.40	10.90	14.44	17.40	6.60	2.86

A silica gel for general commercial catalytic and adsorption purposes prepared by the Davison Chemical Company of Baltimore was tested on ethyl alcohol for comparison purposes. Taste revealed the presence of sodium sulphate in this gel but the quantity present was not determined. Thirty-five grams of the gel in fragments of about 0.3 cm. diameter were used as a catalyst charge. The results obtained with ethyl alcohol and ammonia (Molal ratio 1:1.5 at a flow rate of one mole EtOH per 5.6 hrs.) are given in Table X,

Table X

Temp.	354°	375°	402°	426°	454°	481°
% Amines	5.28	6.80	9.47	10.21	9.44	9.54

whereby it is seen that its efficiency falls far short of that of the active silica gel prepared in the laboratory.

Summary

The alkylation of ammonia by methyl, ethyl, n-propyl, and n-butyl alcohols, by passing their vapors with ammonia over catalysts at 300-500°, has been studied quantitatively. The following catalysts, arranged in the order of ascending effectiveness, have been studied: blue oxide of tungsten, com'l silica gel, alumina, silica gel impregnated with nickel oxide, zirconia, silica gel impregnated with thoria, and special silica gel.

For high activity, long life, and absence of side reactions, the special silica gel has been found to be much the best. The optimum temperatures, percentages of alcohol converted to amines, and the ratios of primary, secondary, and tertiary amines formed are as follows: methyl, 480°, 56%. 5:12:3; ethyl, 465°, 39.5%, 2:5:3; n-propyl, 415°, 49%, 10:11:8; n-butyl, 430°, 25%, 11:11:3.

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THE CATALYTIC DEHYDRATION OF ALCOHOLS[1]

BY A. B. BROWN AND E. EMMET REID

It has long been known that alcohols undergo thermal decomposition in two ways[2]:

$$RCH_2CH_2OH \longrightarrow RCH{:}CH_2 + H_2O$$
$$RCH_2CH_2OH \longrightarrow RCH_2CHO + H_2$$

Both of these reactions are greatly accelerated by catalysts as has been shown in comprehensive studies by Sabatier and Senderens[3] and Sabatier and Mailhe[4]. Sabatier[5] divides the catalysts into 3 classes: (1) dehydrating, (2) mixed and (3) dehydrogenating, placing the oxides of thorium, tungsten, and aluminum in the first class and silica in the second. Kramer and Reid[6] have reported the formation of a large amount aldehyde when butyl alcohol and hydrogen sulphide are passed over thoria and Brown and Reid[7] observed considerable aldehyde formation in the case of butyl alcohol and ammonia over the same catalyst. The question arose whether the aldehyde formation is influenced by the presence of the hydrogen sulphide and ammonia or whether thoria is more of a dehydrogenation catalyst than has been suspected. The recent work of Adkins[8] shows that the method of preparation of a catalyst influences the kind of its action as well as its activity.

As a search of the literature did not reveal complete analysis of the gases evolved in the passage of an alcohol over catalysts for an extended temperature range, it was decided to make a careful study of two alcohols, ethyl and butyl, over the dehydrating catalysts, thoria, alumina, blue oxide of tungsten and silica gel at various temperatures. In all cases carbon dioxide was found: the amounts are small except with thoria with which it is 10% of the reaction product at high temperatures. Its origin is not apparent: perhaps the aldehyde first formed polymerizes to the ester which decomposes to give carbon dioxide in the known manner, or perhaps the carbon monoxide resulting from the breaking up of the aldehyde yields carbon and carbon dioxide.

From ethyl alcohol both ethane and methane are formed and from butyl alcohol, both butane and propane, the amounts of the ethane and butane being particularly large with silica gel as catalyst. The methane and propane doubtless come from the decomposition of the aldehydes yielding CO as the other product, while the ethane and butane must be produced by the hydrogenation of ethylene and butylene by the hydrogen present.

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[1] Contribution from the Chemical Laboratory of Johns Hopkins University.

[2] Berthelot and Jungfleisch: Traité élém. de chimie org. 1, 256 (1886).

[3] Ann. chim. phys. [8] 4, 458 (1905).

[4] Ibid [8] 20, 289 (1910).

[5] "Catalysis in Organic Chemistry," p. 252 (1922)

[6] J. Am. Chem. Soc. 43, 880 (1921).

[7] J. Phys. Chem. 28, 1067 (1924).

[8] J. Am. Chem. Soc. 44, 2175 (1922).

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After our work was finished an article appeared by Gilfillan[1] in which the dehydration of ethyl alcohol by some of the same catalysts is described. His reaction tube was nearly the same size as ours but contained more catalyst and he passed the alcohol more rapidly. Our results agree in a general way with his, in so far as comparisons can be made. He does not give complete analyses of the gases produced.

We find that butyl alcohol is decomposed at a lower temperature than ethyl, the differences for 60% decomposition being 78° with W_2O_5, 104° with alumina, 54° with thoria and 78° with silica gel. Comparing the catalysts, we find the following order with the two alcohols, the figures interposed representing the difference in temperatures at which the catalysts effect 60% decomposition, *i.e.* alumina decomposes 60% of butyl alcohol 27° lower than blue oxide of tungsten:

Ethyl alumina 1° W_2O_5 92° thoria 33° s. gel — s. gel com'l.
Butyl " 27° " 16° " 9° " 81° "

The curves for alumina and blue oxide of tungsten cross for both alcohols. These are the best catalysts for making ethylene and butylene, both on account of high yield and purity of products.

The ratio of unsaturated hydrocarbon to aldehyde decreases with rise of temperature with all of the catalysts. It is greatest with alumina and least with thoria.

Comparing the two alcohols, we find the ratio of butylene to aldehyde to be considerably higher than that of ethylene to aldehyde with the same catalyst.

Catalysts

The preparations of catalysts were similar to those in our study of the alkylation of ammonia[2]. The tube was filled with 75 g. of the special silica gel. The thoria (25 g.) on asbestos was similar to "catalyst A". The blue oxide of tungsten was 75 g. of the commercial oxide made into a paste and suspended on asbestos, otherwise similar to "catalyst F". The alumina catalyst was made by suspending 25 g. of the well washed hydroxide as a paste on asbestos fibre, drying at 100° till crumbly and finally heating in the tube for an hour at 375-400°.

Apparatus

The apparatus used was essentially that described by Kramer and Reid[3] and used by us in previous work[4]. The alcohol fed in through a calibrated dropper at a known rate, approximately 0.2 mole per hour, passed through a vaporizing bulb, over the catalyst and through an air condenser to the receiver, a constant level trap being used to avoid correction for volume of liquid condensed. The air condenser was used to minimize the solubility of the hydrocarbons in the condensate.

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[1] J. Am. Chem. Soc., 44, 1323 (1922).
[2] J. Phys. Chem. 28, 1067 (1924).
[3] J. Am. Chem. Soc. 43, 880 (1921).
[4] J. Phys. Chem. 28, 1067 (1924).

Analysis

The gases were collected in a burette over water saturated with ethylene (or butylene) and analyzed in a modified Orsat apparatus. The steps were: (A) shaking with water saturated with the hydrocarbon to remove alcohol and ether vapors, (B) shaking with caustic potash solution which had been saturated with the hydrocarbon, C_nH_{2n}, (C) shaking with fuming sulphuric acid followed by caustic potash solution containing no C_nH_{2n}, (while the gas sample was in the acid pipette, the burette was filled with water free from the hydrocarbons), (D) shaking with ammonical cuprous chloride, (E) burning the residual gas in a combustion pipette with an oxygen-air mixture, (F) measurement of the contraction due to the combustion, (G) determining the carbon dioxide thus formed.

The Alcohols

Both alcohols were refluxed over lime until thoroughly anhydrous and distilled.

Results

The results are given in Tables I and II. The figures in column 3 are the yield of ethylene or butylene based on the total alcohol passed in while those in the rest of the columns are figured on the amount of alcohol, decomposed as given in column 2. The methane or butane formed is the same as the carbon monoxide. The figures in the last column give the ratio of the ethylene or butylene to the aldehyde found. The percentages of carbon dioxide given are double the percentages found by analysis since two molecules of alcohol are required to give one of the dioxide. The percentages of aldehyde and of aldehyde decomposed have been calculated from data in columns 7 to 10.

TABLE I—ETHYL ALCOHOL

Alumina

Temp.	%Dec.	%C_2H_4	%C_2H_4	%Ald.	%Ald.dec.	%H_2	%CO	%CO_2	%C_2H_6	Ratio
275	21.1	19.9	94.7	1.79	48.0	1.32	0.85	3.29	0.39	52.3
325	70.9	69.0	97.2	1.31	40.0	0.27	0.53	1.06	1.05	78.2
400	86.5	83.4	96.5	2.49	16.2	1.04	0.40	0.93	1.45	38.6
500	86.0	80.9	94.0	4.18	8.0	3.42	0.34	1.99	0.77	22.5

Thoria

350	11.8	8.4	71.7	26.7	3.5	23.8	0.87	3.7	0.98	2.68
400	57.9	36.2	62.6	29.7	5.7	28.7	1.69	8.9	0.98	2.11
450	79.2	41.2	52.1	37.6	5.1	34.7	1.95	15.5	1.25	1.42
500	86.8	39.9	46.0	41.1	3.2	38.9	1.32	19.7	2.38	1.12

(Table I continued on page 1080)

Blue oxide of Tungsten										
250	16.2	15.6	96.1	—	—	—	0.54	2.04	—	—
300	58.9	57.8	98.1	—	—	—	0.39	0.52	—	—
375	65.0	62.8	96.6	2.23	17.7	1.06	0.36	0.48	1.18	43.3
475	70.0	63.5	90.8	8.43	4.0	5.24	0.34	0.64	3.19	10.8
Silica gel, special										
360	16.2	13.7	84.5	14.3	0.0	7.42	0.0	1.31	6.84	5.92
400	47.9	39.5	82.6	15.2	4.8	6.55	0.73	1.46	8.72	5.43
450	66.8	52.2	78.1	—	—	—	0.93	1.86	—	—
500	71.9	52.9	73.5	23.6	4.2	12.28	0.99	1.99	11.34	3.11

TABLE II—BUTYL ALCOHOL

Temp.	%Dec.	%C_4H_8	%C_4H_8	%Ald.	%Ald.dec.	%H_2	%CO	%CO_2	%C_4H_{10}	Ratio
175	48.3	47.7	99.1	—	—	—	0.23	1.19	—	—
255	71.9	70.8	98.5	—	—	—	0.35	0.98	—	—
345	79.1	77.3	97.7	—	—	—	0.49	1.94	—	—
450	91.5	88.8	97.1	1.31	32.9	0.87	0.43	1.45	0.43	74.1
Thoria										
325	24.9	23.3	93.6	4.9	7.1	4.3	0.35	1.31	0.66	18.9
370	78.8	74.6	94.6	3.7	8.0	2.9	0.30	2.07	0.74	25.7
415	84.7	77.6	91.7	5.4	7.9	4.3	0.43	4.27	1.11	17.1
455	100.9	57.3	56.8	29.8	4.5	29.5	1.33	16.82	0.26	1.9
Blue oxide of Tungsten										
225	45.9	45.6	99.3	—	—	—	0.18	0.53	—	—
278	87.7	85.3	98.4	—	—	—	—	0.89	—	—
333	85.9	84.4	98.3	—	—	—	0.42	0.84	—	—
400	88.4	83.2	94.1	5.4	5.2	3.82	0.27	0.29	1.47	17.5
Silica gel, special										
325	17.4	17.6	101.3	—	—	—	0.32	1.26	—	—
355	56.1	54.3	96.8	—	—	—	0.50	0.72	—	—
405	85.2	82.5	96.9	—	—	—	0.41	0.79	—	—
475	84.2	76.0	90.3	3.31	5.5	4.20	0.41	1.05	3.22	27.3
Silica gel, com'l										
400	21.3	19.4	90.9	16.3	4.8	9.3	0.78	2.34	7.0	5.56
440	59.9	45.5	76.0	20.9	5.8	12.0	1.21	1.90	8.9	3.64
485	90.2	59.5	66.0	28.3	8.0	17.5	2.27	2.41	10.9	2.34

The results above were plotted and smooth curves drawn. From these the temperatures at which even percentages of the alcohols are decomposed by the various catalysts were taken off. These are given in Table III.

TABLE III

Temperatures at which various percentages of the alcohols are decomposed.

	Ethyl Alcohol				Butyl Alcohol				
%	W_2O_5	Al_2O_3	ThO_2	Silica gel	W_2O_5	Al_2O_3	ThO_2	Silica Spec.	Gel Com'l
20	253	275	359	364	——	——	——	328	—
30	260	283	369	376	——	——	328	335	—
40	269	292	380	389	220	——	335	342	418
50	282	302	392	409	228	179	342	350	429
60	313	312	405	438	235	208	351	360	441
70	480	325	423	490	243	248	360	371	454
80	——	447	448	——	253	358	370	388	470

Summary

The catalytic decomposition of ethyl and butyl alcohols by blue oxide of tungsten, alumina, thoria and silica gel has been studied between 220° and 500°. The first two named are the best catalysts for producing ethylene and butylene both for yields and absence of side reactions. For 60% decomposition the temperature is about 76° lower for butyl than for ethyl alcohol.

Baltimore, Md.

A STUDY OF THE DENSITY OF CARBON

BY H. C. HOWARD AND G. A. HULETT

Introduction

During the war this laboratory was engaged in a study of the physical properties, such as density, pore volume and adsorbtive power, of the active charcoals which were used as absorbents in the gas masks. In the course of this investigation, the interesting fact was observed that the density of these charcoals, determined by evacuation and immersion of the completely evacuated charcoal in a liquid, varied with the liquid which was employed. This curious phenomenon, together with that of 'drift' or increase in the density of the sample with time of immersion, was studied in detail by Cude and Hulett[1] and they concluded that the use of different liquids resulted in varying densities because the liquids penetrate the capillaries of the charcoal to a different degree, that liquid which penetrates the most readily giving the greatest density and vice versa. Working with the liquids water, benzol carbon tetrachloride and carbon bisulfide, they showed that the densities obtained were in the order predicted by the assumption that the extent of penetration is directly proportional to the surface tension of the liquid employed and inversely proportional to its viscosity.

Assuming that incomplete penetration is the correct explanation of the variation in density observed, it follows that even the highest values obtained for the density by this method are probably lower than the true density. The highest value obtained by Cude and Hulett for coconut charcoal was 1.98.

Harkins and Ewing[2] have also reported the results of density determinations upon active charcoals in several liquids. They observed this same variation in the density of the charcoal in the different liquids but interpreted the results very differently, for they concluded that the variation in density is not due to differences in the degree of penetration of the charcoal by the liquid but to the fact that the liquid at the surface of the charcoal is compressed, and that the magnitude of this compression varies, it being greatest with the most compressible liquid. Obviously the density will appear to be greatest in that liquid which is most highly compressed and densities obtained by a liquid immersion method will, on the basis of this hypothesis, be HIGHER than the true density, (unless there is present a combination of the two effects, incomplete penetration and compression of the liquid). From data on the adsorption of liquids such as benzol, water and ether, these workers concluded that the true density of active charcoal is about 1.6.

Lamb and Coolidge[3] in an article on the heat of adsorption of vapors on active charcoal state, "the process of adsorption can be pictured as taking

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[1] J. Am. Chem. Soc., 42, 391 (1920).

[2] J. Am. Chem. Soc., 43, 1787 (1921).

[3] J. Am. Chem. Soc., 42, 1146 (1920).

place in two steps; first, compression of the gas to such a point that liquifaction ensues, and second, a *further compression of this liquid* by the adsorptive forces of the adsorbent". It is evident that these authors also believe that the density of a liquid film on an adsorbing surface is greater than the density of the liquid in bulk.

A. M. Williams[1] on the basis of experimental work of his own, as well as the data of Cude and Hulett, arrived at the same conclusion. The same author, in another paper[2], again discusses the compression of liquids at liquid-solid interfaces and by plotting the data of Harkins and Ewing[3] and extrapolating, he shows that the specific volume of their charcoal is approximately .69, which corresponds to a density of 1.45. He points out, however, that extrapolation to zero compressibility is probably not justified, because of the comparatively narrow range of compressibility of the liquids employed.

Washburn, in an investigation on the porosity of ceramic bodies[4], was confronted by this same problem of the determination of the true density of porous materials. He employed helium, hydrogen, air, water and vaseline as filling fluids. In most cases the porosities determined by the use of helium, hydrogen and air were identical, thus showing that these ceramic bodies do not adsorb even air in appreciable amounts. In a few of the experiments, however, there was a difference of 1 to 2 percent between the porosity determined by hydrogen or helium and that determined by the use of air; indicating that some of these materials do have slight adsorptive power. Even in the cases where adsorption was thus shown to be present, the porosity, as determined by a liquid, was from 5 to 10 per cent below that determined by the use of helium or hydrogen. That is: although, we are here dealing with an active substance, one that adsorbs air, determinations of the density, using a liquid filling fluid, yield *low* results due to incomplete penetration.

A recent paper by two German workers, Berl and Urban[5] deals with this problem of the effect of the filling fluid on the apparent density of a porous body. In describing their work on the properties of silicic acid gel, these authors state, that ether, not water was used as a filling fluid in making the density determinations, because many small capillaries would have remained closed to the appreciably more viscous water which were readily filled by the ether. As a consequence, they point out, that their values are in all cases higher than older results, which were obtained by the use of water. Obviously these authors believe that the higher density obtained with ether is to be ascribed to the more complete penetration of the capillary spaces of the silicic acid gel by that liquid.

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[1] Proc. Roy. Soc., 98A, 223 (1920).

[2] Trans. Faraday Soc., IV, 1, 87 (1922).

[3] Compressibility, at 12,000 Kg. per square centimeter, for each liquid was plotted against specific volume of the charcoal as observed with that liquid.

[4] J. Am. Ceram. Soc., 1921-1922.

[5] Z. angew. Chem. 36, 57 (1923).

Purpose of the Investigation

It is evident from the preceding discussion that there are possible two distinct explanations of the fact, that the density of a porous body, determined by immersion in a liquid, varies with the liquid employed, and that very different conclusions as to the true density of the body will be reached, depending upon which of these explanations is accepted. The purpose of this investigation was to obtain evidence bearing on these two points of view.

Discussion of Methods

In the determination of the true density of a body such as charcoal, parts of which are difficultly accessible to the filling fluid, the use of a gas as a filling fluid at once suggests itself, since, by its use, surface tension and viscosity effects will be largely eliminated. Unfortunately, all gases, with the possible exception of helium are known to be adsorbed by active charcoal to such an extent as to render them useless for this purpose.

A search of the literature revealed very little exact information as to the magnitude of the adsorption of helium on charcoal. Homfray[1] however, records some experiments and reports that it is not adsorbed at all at room temperatures, but this measurement may be in error by several tenths of a cubic centimeter, since the 'free space' in the system was determined by calculation, from the weight and density of the charcoal employed.

Homfray and several other investigators have also measured the adsorption of helium on charcoal at liquid air temperatures and have found it to be very small as compared even with hydrogen[2], as is shown in the following table:

Adsorption of Hydrogen and Helium at Low Temperatures

	Adsorption	Temperature	Pressure	Observer
Hydrogen	56.0 cc.	−195°C.	20.6 mm.	Claude
Helium	0.21	−195	27	Claude
Helium	1.8	−190	705	Homfray
Helium	.16	−79	674	Homfray
Hydrogen	5.4	−79	721	Titoff

Washburn[3] in speaking of the use of gases in determining density, states, "For most ceramic bodies dry air is a satisfactory gas but hydrogen will be required in some instances. Helium could, of course, be employed for *all* types of porous material at room temperature or above".

The first part of this investigation consisted of measurements of the densities of various carbons at room temperature, using helium as a filling fluid. In computing the density the assumption was made that this gas is not adsorbed. In the latter part of the paper, evidence as to the correctness of this assumption, is submitted.

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[1] Z. physik. Chem., **74**, 129 (1910).

[2] Claude: Compt. rend, **158**, 861 (1914); McLean: Trans. Roy. Soc. Canada, **12**, 79 (1918).

[3] J. Am. Ceram. Soc. **5**, 113 (1922).

Experimental

The apparatus used in the density determinations is shown in Fig. 1. and consisted of a bulb A to hold the charcoal, connected through a ground joint D and a three-way stop cock C to a burette B. This cock also permitted communication with a vacuum pump and a source of helium. In order that the apparatus might be sufficiently compact to be placed in a thermostat, a burette of the weighing type was employed. A 2 mm. capillary tube E connected the lower end of the burette, through a stop cock F with mercury in the weighing bottle G. Communication between the burette and the weighing bottle was controlled by this cock. The weighing bottle was connected to the capillary by an air-tight ground joint. The pressure on the surface of the mercury in the weighing bottle could be regulated through the side tube I, by means of the mercury reservoir L and leveling bottle K. By increasing the air pressure on the surface of the mercury in G, mercury could be forced from the weighing bottle up into the burette and vice versa; the cock F being open, of course, during this procedure.

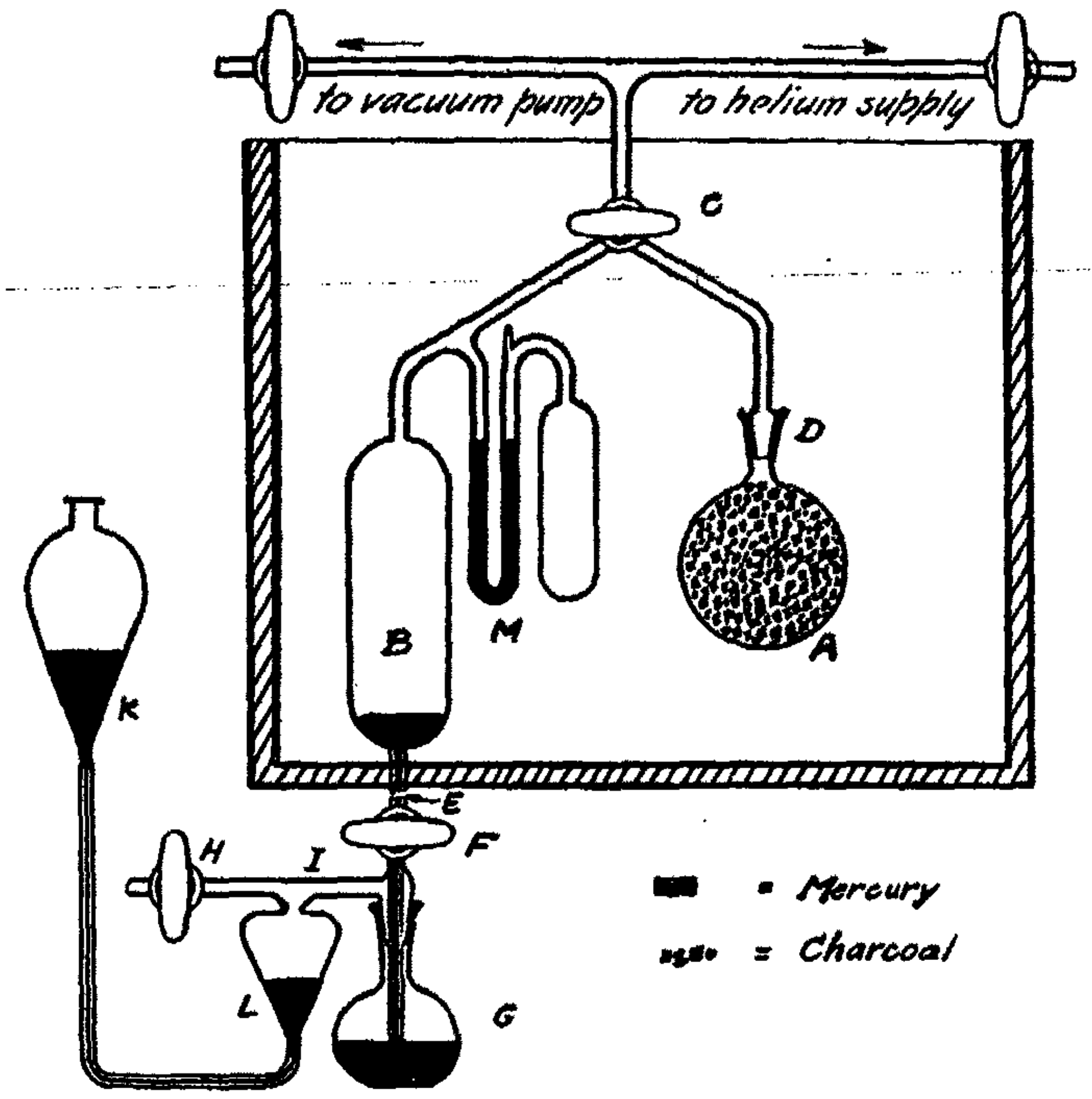

Fig. 1

In order to make a density determination with this apparatus, it is necessary to determine, first, the volume of gas required to fill bulb A and the communicating capillary, when empty, V_1 and, second, the volume necessary to fill it when it contains a known weight of the charcoal, V_2. Assuming that the gas used is not adsorbed by the charcoal, the true density of the latter will be given by the following relation:

$$\text{Density} = \frac{\text{weight of charcoal}}{V_1 - V_2}$$

Method of Manipulation

The bulb A was filled with the sample, which was previously dried in vacuum at 200° C. to remove adsorbed water. The ground joint D was lightly greased and the bulb attached. (In order to permit the sample to be heated during evacuation, the thermostat was constructed so that it could be lowered and swung to one side and an electric furnace placed around the charcoal bulb. During this heating the ground joint at D was kept cool by a few coils of fine lead pipe carrying cold water.). To insure complete removal of adsorbed gases, the samples were first evacuated for four hours at 300-400° C. with a "Hyvac" oil pump, and then with a Toepler pump, until a vacuum of approximately 10^{-3} mm. was maintained over a five minute period. After evacuation the stop-cock C was turned to the right to shut off communication with the vacuum pump and the bulb A was allowed to cool to room temperature. The thermostat was then raised until the burette B and the bulb A were completely immersed.

Stop-cock H was closed and the leveling bottle K raised until it was approximately level with the mercury in the burette B which had been previously filled with purified helium[1]. Stop-cock F was then opened and by varying the height of the leveling bottle the pressure was adjusted to some fixed point on the mannometer M.[2] Stop-cock F is then closed, the levling bottle K lowered, stop-cock H opened, and the weighing bottle G detached and weighed. This procedure was repeated several times. It was found that the pressure settings could readily be reproduced so that the variation from the mean, of the weight of mercury in the weighing bottle did not exceed 0.08 grams, corresponding to a variation of about 0.005 cc. in the volume of gas in the burette.

The volume of the empty bulb once having been found, obviously, all that is required in making a density determination is a measurement of the volume of gas necessary to fill the bulb when it contains a known weight of charcoal.

The "block" density of active coconut charcoal is approximately 0.5 so that about 20 gms. of charcoal will be required to fill a 40 cc. bulb. The free space will be approximately 30 cc. which can be measured with an accuracy of about ±.005 cc. The volume of the charcoal will be approximately 10 cc. and this quantity will be accurate to about ±.01 cc. which will result in an error of four in the third decimal place in the density of a charcoal of this

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[1] The helium used in this work was obtained through the courtesy of Dr. R. B. Moore of the Bureau of Mines. It was purified by first passing over copper and copper oxide at 500°C., and then over freshly evacuated active charcoal at the temperature of liquid air.

[2] A platinum wire, ground to a point, sealed through the side of the mannometer and bent downward at an angle of 90°, was found to be a suitable reference point.

kind. It is evident that the accuracy of the determination depends upon the "block" density of the sample, the smaller the ratio of the block density to the true density, the less the accuracy will be.

The weight of the charcoal used, was obtained after the density determination had been completed, by detaching the charcoal bulb, filled with helium, stoppering quickly and weighing. The data from a determination are given in the following table:

Sample = Coconut charcoal, A909, 20-40 mesh.
Temperature = 25°C. ±.02°. Pressure approximately 76 cm.
Corrected weight of charcoal = 20.57 gms.
Volume of the empty system = 39.03 cc.

A	B	C	D	E	F
	723.73				
0.0	[1]328.60	395.13 gms.	29.19 cc	9.84 cc	2.09
0.3	327.35	396.38	29.35	9.68	2.12
5.5	326.10	397.63	29.38	9.65	2.13
19.0	325.00	398.73	29.46	9.57	2.15
72.0	324.95	398.78	29.46	9.57	2.15

A = Time in hours
B = Weighing bottle and mercury
C = Loss in weight of weighing bottle
D = Volume of helium required to fill the bulb
E = Volume of charcoal
F = Density of Charcoal.

It will be noticed that there is a very distinct "drift" or increase with time, of the volume of helium required to fill the bulb. Cude and Hulett observed this phenomenon when making density determinations with liquids.

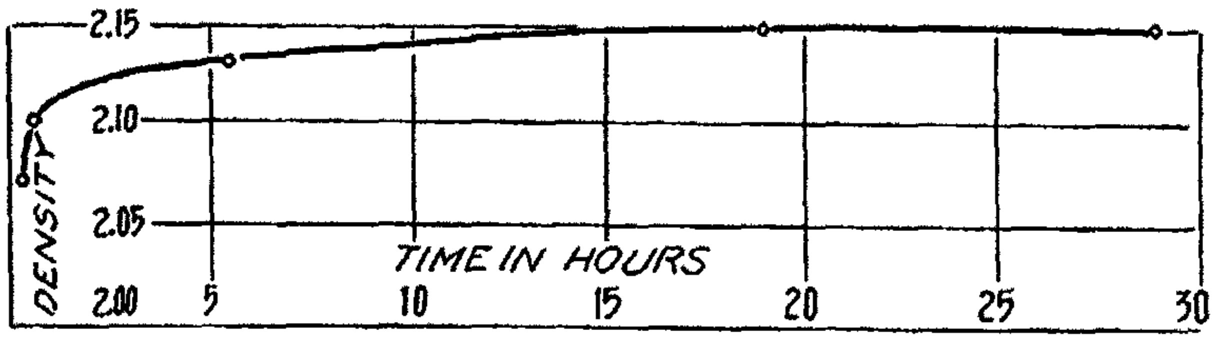

FIG. 2

That it should also be present when a gas is used as a filling fluid, is striking proof of the extreme fineness of the capillary spaces with which we have to deal in a substance like charcoal. The capillaries in such material undoubtedly range in size from those visible to the naked eye to those of atomic dimensions.

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[1] The first reading was taken about five minutes after the stopcock to the evacuated sample had been opened.

The magnitude of the effect is clearly shown in Fig. 2.

The densities recorded for the charcoals which showed this "drift," are those obtained after about twenty hours "soaking" in helium, under a pressure a few millimeters greater than atmospheric.

In order to get an idea of the relative activities or adsorptive capacities of the various forms of carbon upon which these density determinations were made, adsorption measurements with nitrogen were also carried out in each case. In calculating the adsorption, the assumption was made that the volume of helium required to fill the bulb represents the true "free space" of the system.

The results of these density and adsorption measurements are presented in the following table:

	Sample	Density	Nitrogen Adsorption
1	Coconut charcoal A909	2.12	8.8 cc.
2	Sugar charcoal	2.26	6.2 cc.
3	Kelp charcoal	2.28	5.2 cc.
4	Carbon black	2.05	5.5 cc.
5	Coconut charcoal	2.14	8.2 cc.
6	Willow charcoal	1.44	2.8 cc.
7	Petroleum coke	1.43	0.3 cc.
8	Coke from bituminous coal	1.51	0.5 cc.
9	Ceylon graphite	2.28	None

The nitrogen adsorption is given in cc. of nitrogen, reduced to N. T. P., per gram of charcoal.

All the samples were 20 to 40 mesh, except the kelp charcoal and the carbon black, which were finer than 100 mesh. A brief description of each of the samples is given below.

1. A steam activated coconut charcoal.
2. Prepared by igniting recrystallized cane sugar in an open dish and then heating the resulting charcoal for four hours at 1000°C. in vacuum.
3. A decolorizing charcoal from the Government Plant in California. It contained about twelve percent ash.
4. A steam treated gas black.
5. An active coconot charcoal from the National Carbon Company.
6. A laboratory charcoal such as is used for "blowpipe" analysis.
7. From the stills of the Standard Oil Company, Bayonne, New Jersey.
8. From Illinois soft coal—Coke "E" from the Bureau of Mines.

Discussion of Results

It will be observed that the densities of these carbons, with the exception of those which were probably very imperfectly freed from hydrocarbons, are nearly the same as that of graphite. Chaney[1] has reported that the densities of active charcoals, determined by evacuation under kerosene, approach that

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[1] Trans. Am. Electrochem Soc. 36, 107 (1920).

of graphite. The value found by Harkins and Ewing, using ether as a filling fluid, was 2.129. In this connection, a paper by Debye and Scherrer[1] is of interest. They concluded from X-ray analysis, that there was no essential difference between amorphous carbon and graphite, the amorphous carbon being merely in a finer state of subdivision, and recently, G. Asahara[2], from a series of similar experiments has reached the same conclusion.

The Problem of the Adsorption of Helium

As was previously pointed out, these density determinations with helium are based on the assumption that the gas is not appreciably adsorbed by charcoal at room temperature. If the helium *is* adsorbed, we can readily calculate the magnitude of the adsorption which must be present to give a body of true density of the order of 1.5, an apparent density of 2.0. It will evidently be represented by the difference between the specific volumes 0.66 and 0.50 or 0.16+cc. per gram.

Measurement of adsorption of this order of magnitude, or absolute proof of its absence is not a simple problem, but the well known variations of adsorption with (1) temperature, and (2) pressure, suggest an opening for attack, as does also the fact, (3) that the ratio of the adsorptive powers of two charcoals of different degrees of activity is approximately constant for all gases. That is, if the adsorptive power of a charcoal for nitrogen is largely destroyed, its adsorptive power for helium will be decreased in a similar ratio.[3]

The three possible means of solution of the problem, which were suggested above, will now be considered in detail:

(1) Variation of Adsorption with Temperature:—By reference to Fig. 1. it can readily be seen that, since the bulb "A" and burette "B" are both at the same temperature, the volume of gas required to fill "A" is independent of temperature, if no adsorption takes place and the thermal expansion of the bulb itself is neglected.

If, however, the bulb "B" is filled with an adsorbing material, the amount of gas necessary to fill the bulb will not be independent of the temperature.

Let us consider the volume of gas required to fill a given bulb containing an active material at two temperatures, such as t_1 and t_2. Then if: V_1 = volume required to fill the bulb at t_1,

V_2 = volume required to fill the bulb at t_2.

a_1 and a_2 = the adsorptions in cc. per gram corresponding to t_1 and t_2, (reduced to N. T. P.).

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[1] Phys. Z. **18**, 291 (1917).

[2] Chem. Abstracts, **17**, 656 (1923).

[3] See Freundlich: "Kapillarchemie", p. 178 (1922).

It is interesting to note that in this last respect, active charcoal differs markedly from metals such as copper. See Pease: J. Am. Chem. Soc., **45**, 1207 (1923).

Sheldon (Phys. Rev. **16**, 165 (1920) has reported a charcoal which varied from the usual mode of behavior, in that its relative adsorptive power for nitrogen and hydrogen could be *reversed* by suitable treatment.

V_B = the volume of the bulb,
M = the mass of the charcoal,
and d = the true density of the charcoal

the following relationships will evidently hold

$$\text{(a)}\ V_1 = V_B - \frac{M}{d} + a_1M\left(\frac{273+t_1}{273}\right)$$

$$\text{(b)}\ V_2 = V_B - \frac{M}{d} + a_2M\left(\frac{273+t_2}{273}\right)$$

$$\text{(c) and } V_1 - V_2 = a_1M\left(\frac{273+t_1}{273}\right) - a_2M\left(\frac{273+t_2}{273}\right)$$

From equation (c), it follows that for $V_1 - V_2$ to be zero, a_1 and a_2 must be zero or the condition $a_2 = \left(\frac{273+t_1}{273+t_2}\right)a_1$ be fulfilled. In other words, *unless* the change of adsorption with temperature *happens* to be of the same or nearly the same order as the change in density of the gas with temperature, a zero value for $V_1 - V_2$ shows that the adsorptions at t_1 and t_2 are zero, within the limits of experimental error.

Experimental

Measurements of the volume of helium required to fill the bulb A when empty and when containing coconut charcoal, were made at 25°, 50°, and 75°C. The pressure in each case was approximately 760 mm. The results of these measurements are presented in the following table.

(a) Volume of helium required to fill the empty bulb at:—

	25°	50°	75°
	39.093	39.090	39.088
	39.088	39.098	39.095
	39.100	39.087	39.099
Mean =	39.090 cc.	39.091 cc.	39.094 cc.

(b) Volume of helium required to fill the same bulb containing 20.671 gm. of coconut charcoal,—

	25°	50°	75°
	29.137	29.134	29.151
	29.150	29.125	29.138
	29.140	29.144	29.129
Mean =	29.142	29.134	29.139

These data indicate that helium is not adsorbed measurably at 25° and above.

(2) Variation of Adsorption with Pressure:—In general, the adsorption of gases on charcoal increases with pressure. With some gases, e.g., hydrogen, the increase is approximately a linear function, with others, such as nitrogen, the variation is exponential. By carrying out a series of experiments at constant temperature and varying pressure, and by the application of equations

analogous to those developed above, further evidence as to the magnitude of the adsorption could be obtained. It was not found possible to investigate this phase of the problem.

(3) Destruction of Adsorptive Power and Measurement of the Density of the Inactive Charcoal:—If the nitrogen adsorption of a charcoal of known density is decreased by some means to a fraction of its original value and the density of the charcoal (measured with helium), remains unchanged, we are justified in assuming that the adsorption of helium by the original charcoal is negligible, since, as pointed out above, the ratio of the adsorptive powers of two charcoals is approximately constant for different gases[1].

It is well known that, in general, heating tends to decrease the adsorptive power of active materials. The temperature required varying greatly with different substances. Lemon[2] has reported that the adsorptive power of coconut charcoal can be greatly decreased by evacuating at 900°C. and completely destroyed at 1200°C. These results suggested the possibility of destroying the activity of our charcoal by heating to a high temperature in vacuum. Then by measuring the density of the active and inactive charcoal with helium, we would obtain information as to the magnitude of the helium adsorption and consequently, evidence asto the correctness of our density determinations.

Preliminary experiments showed that we could decrease the adsorptive power of our charcoal for nitrogen to approximately half its original value by heating for an hour under vacuum in a quartz tube to 1100°-1200°C. Because of the short life of the quartz tubes at this temperature and the possibility of the contamination of the charcoal, we later employed alundum tubes.

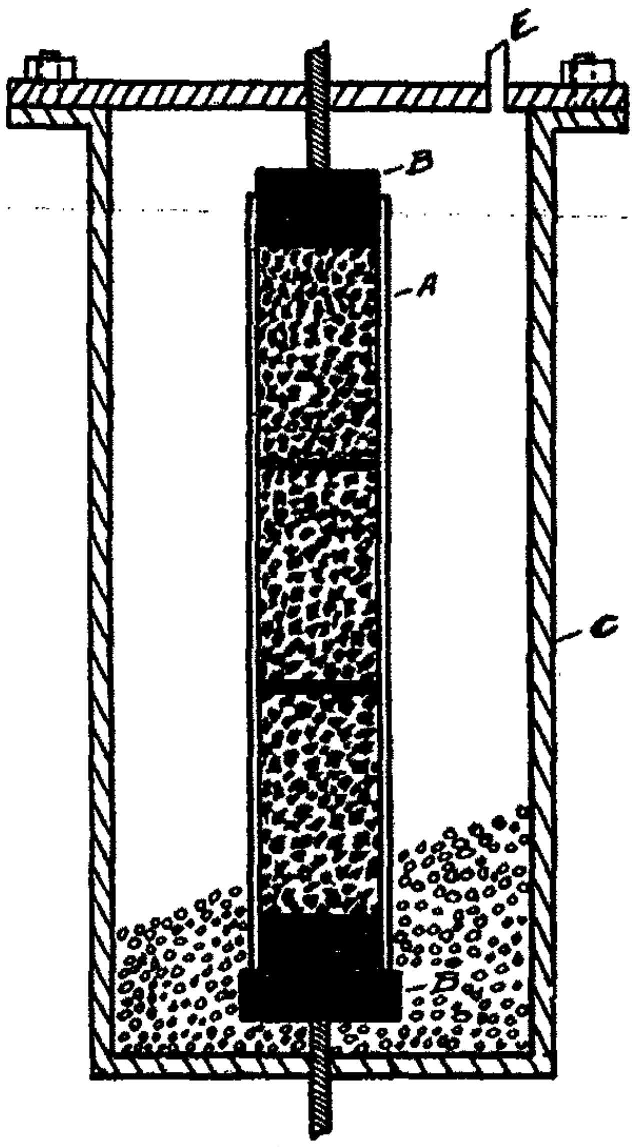

FIG 3
Charcoal inside the tube; Magnesium Oxide outside

The apparatus which we found most satisfactory for the heating of charcoal to high temperatures in vacuum is shown in Fig. 3. A is an alundum tube, B and B[1] are graphite electrodes, C is an iron vacuum-tight jacket fitted with a cover plate D. The system was evacuated through E. The leads from the electrodes were insulated and water-cooled and, to prevent radiation, the space around the alundum tube was packed with 10-mesh, fused magnesium oxide. The charcoal was placed inside the alundum tube.

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[1] Obviously, in computing these nitrogen adsorptions, it is immaterial whether the charcoal is assumed to have a density of 1.5 or 2.0, since the difference involved is of another order of magnitude entirely.

[2] Phys. Rev., **14**, 281 (1919).

Because of the large temperature gradient between the electrodes, it was found necessary to introduce two graphite discs dividing the charge approximately into thirds. By this means the central portion could be separated cleanly and the upper and lower thirds discarded. The temperature of the central portion was taken by a thermocouple encased in a small alundum tube, introduced through the side of the large alundum tube.

The electrical conductivity of the coconut charcoal was found to be such that the application of 220 volts on the end of the charge heated the central portion of the charcoal to 1200° in about half an hour and 3 to 4 amperes were found to be sufficient to maintain it at that temperature indefinitely.

The effect of heat treatment on the density and adsorptive power of coconut charcoal is shown by the following data:—

	Temperature	Density	Nitrogen Adsorption
(1)	900°-1000°C	2.22	8.2 cc.
(2)	1100°-1200°C	2.26	3.9 cc.
(3)	1300°-1400°C	2.13	3.8 cc.
(4)	Approx. 1600°C	1.44	0.2 cc.
(5)	Approx. 2000°C	1.35	0.2 cc.

Nitrogen adsorption is given in cc. per gram at N. T. P.

The samples were maintained at the temperatures indicated for 30 minutes. Temperatures up to 1400° were measured with a Pt-Pt.Rd thermocouple. Charcoals (4) and (5) were not heated in this furnace but in a covered graphite crucible in a Northrup induction furnace. (The temperatures in (4) and (5) were estimated by the operator of the furnace.[1]

The results obtained in runs (1), (2) are such as would be predicted from general considerations. There is a marked decrease in adsorptive power and a slight increase in density as the temperature of treatment is increased.[2] These data indicate that our original assumption, with respect to the non-adsorption of helium, is correct.

The data on density and adsorption, for the charcoals which were heated to 1600° and 2000°C., appear to refute this statement. It seems probable, however, that the values given do not represent the true densities of these charcoals. Such abnormally low densities would evidently be found if a large portion of the inner spaces of the charcoal had been cut off from communication with the exterior by a "plugging" of the fine capillaries, with carbon deposited from the "cracking" of hydrocarbons. In this connection, the marked difference in appearance noted between charcoals (1), (2), and (4), (5) is pertinent. The first two had the usual slight lustre of an active coconut charcoal and the particles were clean and hard. Charcoals (4) and (5), on

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[1] In order to confirm the value 1.44 found for charcoal (4), with helium, a density determination was made in water. The density found by that method was 1.330.

[1] The authors are indebted to Dr. E. F. Northrup for his co-operation in carrying out these latter runs.

[2] See Firth: J. Chem. Soc., **119**, 926 (1921).

the other hand, were dead black and left a sooty deposit when rubbed on paper. Each piece looked as though it had been given a coating of carbon black.[1]

The explanation given above for the abnormally low densities found for charcoals (4) and (5) is further confirmed by the abnormally large "drift" observed in the case of charcoal (3), which was heated to an intermediate temperature and might be expected to exhibit an incomplete stopping of the capillaries. In the case of this charcoal, the *rate* of penetration of the helium was *decreased* remarkably but penetration was not completely prevented.

By comparison of the following curve, Fig 4, with that given before, the much greater magnitude of the drift in this case can readily be seen.

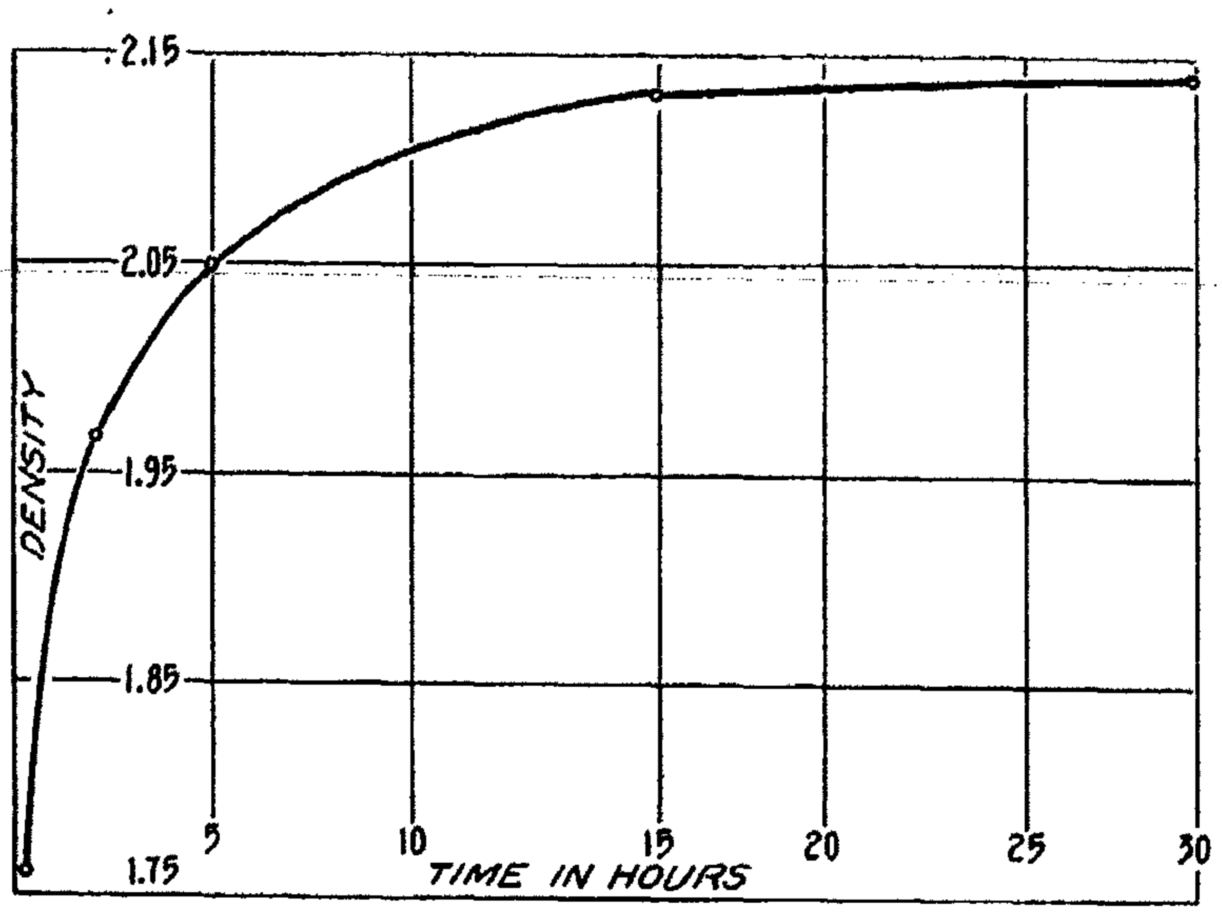

FIG. 4

The work of Berl and Urban, on the properties of silicic acid gel, which has been mentioned in another connection, is also of interest here. In experiments where the gel was heated from 300° to 1000°C. they observed a decrease in apparent density. The explanation which they offer is as follows: "The heating produced an increasing closure of the capillary openings, so that the pore volume was not completely filled by the ether, from which there necessarily followed a decrease in apparent density."

The values which they obtained for the density of silicic acid gels which had undergone the treatments indicated, were as follows:

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[1] That the low values found for charcoals (4) and (5) were not the result of the different method of heating employed with those charcoals, was proven by an experiment in the furnace shown in Fig. 3. During one run, this furnace accidentally reached a temperature such that the thermo-couple melted, indicating a minimum temperature of 1700°-1800°, and the density of the charcoal so treated was found to be 1.42.

Density

2.465	Dried at 25°C.
2.390	Heated at 300°C.
2.271	Heated at 1000°C.

The similarity of their results to those which we obtained with carbon is very striking, the chief difference being the higher temperature at which the effect is observed in the case of carbon.

It was thought desirable to obtain definite proof that the charcoals with which we were dealing followed the relationship discussed under (3), which, it will be recalled, was that charcoals of different degrees of activity exhibit a constant ratio of adsorptive power for different gases.

With this end in view, the following measurements were carried out:—

(a) The adsorptions of carbon dioxide, nitrogen, and hydrogen on active charcoal.

(b) The adsorptions of these gases on the same charcoal after the latter had been heated for thirty minutes at 1200°-1300°C. in vacuum.

The data show that the relationship holds approximately with these gases.

Adsorptions at 25°C

(cc. at N. T. P. per gram of charcoal)

	Carbon Dioxide	Nitrogen	Hydrogen
(a) Active coconut charcoal	51.0	8.2	0.81
(b) Coconut charcoal after heat treatment	25.6	3.9	0.55

While the proof of the absence of adsorption of helium on active charcoal at room temperatures is not so complete as could be desired, the following points are considered to be good evidence that our assumption in that respect is correct.

(1) The volume of helium required to fill a bulb containing active charcoal was found to be the same at three different temperatures.

(2) The density of a charcoal, determined with helium, does not decrease when its activity, as measured by nitrogen adsorption, has been decreased to half its original value.

(3) With carbon from different sources no direct relationship has been found between the density of a charcoal, measured with helium, and its activity. In general, the active charcoals show higher densities, as would be expected, considering their greater freedom from hydrocarbons.

(4) No density determination with helium has yielded a value higher than the density of graphite. If the density measured with helium does not represent the true density of the charcoal, it seems a strange coincidence, that the magnitude of the adsorption should always happen to be such as to yield an apparent density less than that of graphite.

A comparison of our results with those obtained by Harkins and Ewing shows that densities determined with helium are only slightly higher than those obtained by the use of certain liquids such as ether and pentane. If these values are all too high, the error in each case being due to increase in density of the filling fluid at the surface of the charcoal, it seems remarkable that a comparatively highly incompressible fluid, such as ether, should be compressed to almost the same degree as a readily compressible fluid such as helium.

Summary

1. An apparatus has been constructed for the determination of the true density of porous substances. Helium gas is used as the filling fluid. In the case of coconut charcoal, the density can readily be determined with an accuracy of one unit in the second decimal place.

2. The density of active coconut charcoal determined in this way is of the order of 2.1.

3. The values for the density of charcoal found by this method confirm the conclusions of Debye and Scherrer and of Asahara, that all carbons consist essentially of graphite which is contaminated to a greater or less degree with hydrocarbons.

4. The results of density determinations on carbon from various sources show a wide variation, depending upon the purity. Low densities are attributed to the presence of hydrocarbons.

5. Carbons which have been heated above 1400°C. show abnormally low densities.

6. The hypothesis of Harkins and Ewing and of Williams that liquids at the surface of strongly adsorbing solids exist at greater than normal density, has not been confirmed.

7. Evidence is presented to show that the adsorption of helium gas by active charcoal at room temperature is not of sufficient magnitude to vitiate density determinations in which it is employed as a filling fluid.

IRREVERSIBLE REDUCTION AND CATALYTIC HYDROGENATION[1]

BY JAMES B. CONANT AND HAROLD B. CUTTER

Organic compounds which are rapidly reduced in solution by soluble reducing agents may be divided into two classes. In the one class are those substances of which the oxidized and reduced forms are in mobile equilibrium at room temperature with reducing or oxidizing agents, and in the other are compounds whose behavior under ordinary conditions does not correspond to the existence of such equilibria. As examples of the first class may be mentioned the systems, quinone-hydroquinone, indigosulfonate-leuco-indigosulfonate, nitrosobenzene-phenylhydroxylamine in which the relationships between the oxidized and reduced substances are essentially those so common in inorganic chemistry and represented by the system ferric chloride-ferrous chloride. Numerous investigations[2] of the last few years have shown that the oxidation-reduction potentials of such organic systems may be measured and these potentials condition the behavior of the compounds in question towards oxidizing or reducing agents. In almost all cases of such reversible oxidation or reduction, the speed at which equilibrium is attained is very rapid even in dilute solutions at room temperature.

The reduction of compounds of the second class such as azo dyes, nitro compounds, and certain unsaturated ketones also proceeds rapidly, but, unlike the reduction of quinone does not reach a final equilibrium. This is evident from the fact that it is impossible to find a reducing agent with which the reduction will proceed to such a measurable equilibrium (reducing agents either are without effect or cause complete reduction) and also because the reduction can not be reversed by treating the reduced compound with an oxidizing agent of potential higher than that of the weakest reducing agent necessary for the reduction. Thus while 1, 4 naphthoquinone is reduced to the hydroquinone by stannous chloride (potential = +0.4) and the hydroquinone is oxidized to the quinone by ferric chloride (+0.8), dibenzoylethane (C_6H_5-$COCH_2CH_2COC_6H_5$) is not affected by ferric chloride although the oxidized form, dibenzoylethylene, ($C_6H_5COCH = CHCOC_6H_5$) is not reduced by stannous chloride but only by the more powerful titanous chloride (+0.0). We shall designate the reduction of a substance of this second class by the term *irreversible*, in order to distinguish it from the reversible reduction of a compound of the first class.

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[1] Contribution from the Chemical Laboratory of Harvard University.

[2] Granger and Nelson: J. Am. Chem. Soc. **43**, 1401 (1921); W. M. Clark: J. Wash. Acad. Sci. **10**, 255 (1920); Public Health Reports **38**, 443, 666, 933, 1669 (1923); Biilmann: Ann. chim. **16**, 321 (1921); **19** 137 (1923); La Mer and Baker: J. Am. Chem. Soc. **44**, 1954 (1922); Conant, Kahn, Fieser and Lutz: Ibid, **44**, 1382 (1922); Conant and Fieser: Ibid, **44**, 2480 (1922); **45**, 2194 (1923).

No oxidation-reduction potential can be measured in the case of a compound which is irreversibly reduced since the oxidized and reduced forms are not in equilibrium with the reducing agents. Thus, while an inert electrode immersed in mixtures of a quinone and the corresponding hydroquinone rapidly attains a definite potential which is a function of the concentrations of the two compounds and the hydrogen ion, no reproduceable potentials can be obtained with mixtures of dibenzoyl-ethylene and dibenzoylethane. It would seem at first sight, therefore, as though it would be impossible to describe quantitatively the conditions limiting the reduction of all those organic compounds which fall in the second class noted above. However, while no real oxidation-reduction potential of such irreversible systems can be formulated or measured, it is possible to characterize them with considerable precision by determining the potential of the weakest reducing agent (i.e. the reducing agent of highest oxidation-reduction potential) which will cause reduction. Thus if a series of reducing agents of known potential are available, it is a relatively simple matter to determine that dibenzoylethylene, for example, is not reduced by reagent A of potential +0.31 but is reduced by B of potential +0.24; some value within this range of +0.31 to +0.24 can be considered as the potential of the critical reducing agent which would just cause appreciable reduction; the potential of such a hypothetical reducing agent we have called the "Apparent Reduction Potential" of the substance in question; in the case of dibenzoylethylene, the value of the apparent reduction potential is +0.27±0.03 volts. In previous papers[1] from this Laboratory we have determined the apparent reduction potential of a variety of organic substances supplementing the usual inorganic reducing agents with certain hydroquinones and similar substances whose potential could be readily measured. The accuracy of the method obviously depends primarily on having a series of reducing agents such that the potential of each member is only slightly less than that of the preceding member; with the reducing agents now available this can be satisfactorily realized within certain ranges and the apparent reduction potential determined within 0.03 of a volt. For compounds which are not reduced by reducing agents of potential +0.150, however, there are relatively few reagents available and the apparent reduction potential is correspondingly uncertain.

The actual experimental procedure is much simplified by using an electrochemical device for determining whether or not a certain reducing agent reacts with the substance in question. This has been done by introducing the substance into an equimolecular mixture of the reducing agent and its oxidized form (e.g. a quinone and the hydroquinone) and noting whether or not the potential of an inert electrode immersed in the mixture changes during a definite time (30 minutes, for example). A slight reaction between the reducing agent and the substance introduced will obviously cause a considerable change in the ratio of the concentrations of the reducing agent and its oxidized form and a corresponding change in potential. With a great

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[1] Conant and Lutz: J. Am. Chem. Soc. 45, 1047 (1923); 46, 1295 (1924)

majority of the substances investigated there was a sharp distinction between the reagent which was without action and the next in the series which caused reduction, since with the latter the reduction process proceeded at such a rate that it was practically complete in 10 minutes or less. In a few instances where it was possible to use a closely graded series of reducing agents, "border line cases" were met which very nearly corresponded to the "critical reducing agent" whose potential would represent the actual apparent reduction potential of the substance under investigation. In such border line cases the reduction proceeded at a relatively slow rate, while a reducing agent of slightly higher potential was without effect, and a reagent of slightly lower potential caused rapid reduction.

Before discussing the probable mechanism of irreversible reduction and the relation of this problem to catalytic hydrogenation, it will be well to consider certain obvious limitations to the quantitative formulation just outlined. Since we are dealing with a reaction which runs to completion, the problem is one of rates of reaction and not of equilibria. The question may, therefore, well be raised as to how much significance can be attached to these apparent reduction potentials. Are these irreversible reductions governed primarily by the potential of the reducing agent? Does it necessarily follow that all reducing agents of potential less than a certain value will reduce the substance in question? May not the whole process be determined by specific properties of the reducing agents and not by their potential? The answer to these questions is a matter of experiment and while the final verdict can not be rendered until all the conceivable cases have been examined, the evidence at present seems very clear. If one specifies the solvent, (in particular the hydrogen ion concentration), and the temperature and defines the term "appreciable reduction" as a few per cent reduction in 30 minutes, the results of experiments in this Laboratory with some 75 compounds of a half dozen types can be summarized in the statement, *under definite experimental conditions the potential of the reducing agent employed determines whether or not appreciable reduction will take place in homogeneous solution*. We have found no exception to this although the reducing agents employed have been as different as titanous chloride, leuco-indigosulfonate and sulfonated anthrahydroquinone. Experiments have been carried out in both aqueous solutions and solutions containing large amounts of acetone or in some cases of alcohol, the use of these organic solvents being necessary with substances insoluble in water. The few compounds which could be investigated in all three solvents (all about 0.1N in HCl) were found to have essentially the same apparent reduction potentials in each solution.

The effect of changes in hydrogen ion concentration (investigated in aqueous buffer solutions) need not be considered in detail in this paper but the results can be summarized by the statement that the concentration of the hydrogen ion affects the process of irreversible reduction in much the same way as it affects the reversible reduction of quinones and similar compounds.

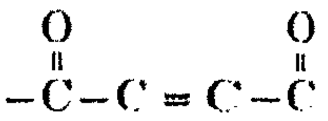
The following table (taken from a previous paper) is of interest as showing the influence of structural changes on the apparent reduction potential: the series of compounds given below all contain the system  $-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{C}=\text{C}-\overset{\text{O}}{\overset{\|}{\text{C}}}$ which is also present in many substances which are reversibly reduced, such as the quinones and indigo. These results were all obtained at 24°±2°, and are, therefore, comparable with each other but not with the action of a reducing agent at some higher or lower temperature. For example, undoubtedly at 100° a substance might be rapidly reduced by a reducing agent of potential higher than the apparent reduction potential determined at 25°. The exact magnitude of this effect of increased temperature has not yet been ascertained.

TABLE I

Apparent Reduction Potentials

Substance	Solvent	App. Red. Pot. (normal hydrogen electrode = 0)
Dibenzoylethylene (cis and trans) ($C_6H_5COCH=CHCOC_6H_5$)	A	+0.27 (±.03)
Benzoylacrylic-acid ($C_6H_5COCH=CHCOOH$)	A	+0.08 (±.06)
Benzoylacrylic acid	B	+0.08 (±.06)
Benzoylacrylic ester($C_6H_5COCH=CHCOOC_2H_5$)	A	+0.08 (±.06)
Maleic ester ($C_2H_5OOCCH=CHCOOC_2H_5$)	A	−.25 (±.10)
Maleic acid	A	−.25 (±.10)
Maleic acid	B	−.25 (±.10)

A = 75% acetone, 25% aqueous hydrochloric acid; total acidity 0.2N.
B = aqueous 0.2N HCl.

Low Temperature Catalytic Hydrogenation

It will be noted from Table I that maleic acid has an apparent reduction potential of −0.25±0.10; it is instantaneously reduced by chromous chloride (−0.40) but is not affected by vanadous chloride (−0.15) even after many hours; it is, however, reduced in dilute hydrochloric acid by hydrogen and colloidal platinum.

The potential of the hydrogen-platinum combination is, obviously, that of the hydrogen electrode and in 0.2N hydrochloric acid is about −.05, a value considerably above the potential of vanadous chloride which is without effect. How is this to be explained? A similar problem was raised in an earlier paper[1] in connection with the reduction of dimethylacrylic acid. This compound is not reduced by chromous chloride but is readily hydrogenated by hydrogen and a catalyst in 0.2N hydrochloric acid at room temperature. We concluded from these previous experiments with dimethylacrylic acid that the process of catalytic hydrogenation, unlike reductions brought about by soluble reducing agents, could not be formulated electrochemically and that

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[1] J. Am. Chem. Soc., **44**, 265 (1922)

probably a different mechanism was involved. We suggested that in the case of a reduction process caused by chromous chloride the addition of electrons and hydrogen ions was involved and in the case of catalytic hydrogenation the direct addition of activated hydrogen atoms.

Bancroft[1] in the Second Report of the Committee on Contact Catalysis has reviewed our earlier paper and has stated that the experiments as they stand are not convincing. He has suggested that it is important to determine whether or not colloidal platinum will catalyze a process of reduction involving a soluble reducing agent. The results of such an experiment with chromous chloride would, however, not be very significant since, as he points out, the catalyst will cause the evolution of hydrogen and reduction must take place unless some catalytic poison is present, as the system gaseous hydrogen + catalyst + dimethyl acrylic acid is known to give isovalerianic acid. A crucial experiment can be carried out, however, with a reducing agent which is not decomposed by colloidal platinum.

An equimolecular mixture of anthrahydroquinone 2,7 disulfonate and anthraquinone 2,7 disulfonate has a potential in 0.1N hydrochloric acid of +0.17; a platinum catalyst is without action on such a mixture. If now maleic acid is introduced into the mixture together with the platinum catalyst it is found that no reduction takes place. That the catalyst is not poisoned can be shown by carrying out the usual process of catalytic hydrogenation with the same solution at the conclusion of the experiment. Similar results were obtained with dimethyl acrylic acid. The experimental details are given below.

In a glass cell of 350 cc. capacity equipped with a stirrer, electrodes, gas inlet and outlet tubes, and connected to a saturated calomel electrode with a saturated KCl bridge, there were placed 100 cc. of vanadous chloride solution, 100 cc. of 0.1 N hydrochloric acid, and 10 cc. of a solution of colloidal platinum. The apparatus was swept out with nitrogen and a solution of anthraquinone 2,7 disulfonate in 0.1N hydrochloric acid was added in such amounts (20 cc. of a 0.05 M solution) that an approximately equimolecular mixture of the anthraquinone and anthrahydroquinone sulfonates resulted; the amount of vanadous chloride being sufficient to reduce only half the added anthraquinone sulfonate. The potential of the bright and platinized electrodes immersed in this mixture were constant for half an hour at +0.184 (on the hydrogen scale); 20 cc. of a 0.1M solution of dimethyl acrylic acid in 0.1M hydrochloric acid was now introduced and the potential of the cell noted over a period of half an hour. There was a change of 2 millivolts in the direction opposite to that which would have been caused by any reduction. If any reduction had occurred there would have been a change of at least 20 millivolts as demonstrated by many experiments in this Laboratory in connection with the determination of apparent reduction potentials. To test whether the catalyst was still active, a quarter of the mixture was shaken with hydrogen in the usual manner after the completion of the above experiment. In the course of

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[1] J. Phys. Chem. 27, 801 (1923).

half an hour 10 cc. of hydrogen was absorbed and a decided odor of isovalerianic acid resulted. To another portion 0.25 g. of dimethyl acrylic acid was added and the mixture shaken with hydrogen; after an hour 40 cc. of hydrogen had been absorbed (theor. am't 58 cc.) and a strong odor of isovalerianic acid was apparent. The catalyst used in this experiment was prepared by the reduction of 3 cc. of a 10% solution of chlorplatinic acid mixed with 7 cc. of 1% gum arabic solution by shaking with hydrogen with one drop of "seeding solution" prepared in the usual manner.[1]

The experiments with maleic acid were performed exactly as above except that in place of the colloidal platinum solution, a suspension of 0.1 g. of a platinum catalyst prepared according to Adams' directions[2] was employed, the platinum oxide being reduced to the active state by shaking with hydrogen before the catalyst was used. After the electrode potential had been constant for 15 minutes at +0.130, 20 cc. of a 0.1M maleic acid solution was added. A change of only one millivolt was noted during the next 30 minutes. To test the catalyst, 0.5 g. of maleic acid was added to 50 cc. of the solution and the mixture shaken with hydrogen. After 90 minutes, 160 cc. of hydrogen had been absorbed (theor. = 120 cc.), the solution was filtered and extracted three times with ether, and the ether layer on evaporation yielded 0.35 g. of succinic acid.

If the process of catalytic hydrogenation is similar to reduction by soluble reducing agents then the catalyst must function not only to make gaseous hydrogen an effective electrochemical reducing agent at room temperature, but also to alter in some way the maleic acid or dimethyl acrylic acid so that it is reduced at a much higher potential than otherwise is the case. In other words, if an electrochemical account of catalytic hydrogenation is to be formulated, we must assume that the apparent reduction potential of maleic acid is much higher (above −0.05) in the presence of a platinum catalyst than in its absence. That some catalyst having such an effect might be found is entirely to be expected; in fact it is readily conceivable that in the presence of the proper catalyst the system maleic acid-succinic acid might be as mobile as the quinone—hydroquinone system. If this is the effect of the platinum catalyst, it should function equally well with other reducing agents (providing it is not "poisoned" which can be determined experimentally). However, the experiments given above show conclusively that platinum does not cause the reduction of either maleic or dimethyl acrylic acid by a reducing agent having a potential only slightly above that of hydrogen itself.

It might be objected that the difference in potential between the reducing agent chosen (+0.17) and hydrogen (−0.05) was sufficient to vitiate any conclusions; it is possible that the energy relationships in the system maleic acid, hydrogen and succinic acid correspond to a true oxidation-reduction potential between these values, for example +0.05. If this were the case, however, and an electrochemical explanation of catalytic hydrogenation

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[1] Skita: Ber. 45, 3589 (1912)

[2] Adams and Vorhees: J. Am. Chem. Soc. 44, 1397 (1922)

correct, an oxidizing agent such as ferric chloride (+0.8) should oxidize succinic acid to maleic acid in the presence of platinum and isovalerianic acid to dimethyl acrylic acid. Such reactions do not proceed as the following experiments show.

The apparatus used was identical with that described above. A 0.01 solution of ferric chloride in 0.1M hydrochloric acid (250 cc.) was introduced into the cell together with 7.5 cc. of a colloidal platinum solution prepared in the usual manner. After the potential had been constant for 30 minutes at +0.838, 7.5 cc. of a 0.1M succinic acid solution was added and a potential change of only 3 millivolts occurred during the half hour. In another experiment with Adams' catalyst the same results were obtained. Similarly when a solution of isovalerianic acid was introduced in another experiment, the potential was constant within a millivolt for 30 minutes. To illustrate the effect on the potential of any action between the ferric chloride and the substance introduced, the following experiment may be mentioned. To 250 cc. of 0.1M ferric chloride and catalyst as above, 7.5 cc. of 0.1M solution of hydroquinone was added. The potential fell from +0.833 to +0.666 within ten seconds after the addition of the hydroquinone. That the ferric chloride had not poisoned the catalyst in the above experiment was demonstrated in each case by taking 30 cc. of the solution after the experiment, adding 0.5 g. of dimethylacrylic acid and shaking with hydrogen; in each case 120 to 160 cc. of hydrogen was absorbed in 90 minutes. (Theor. = 120 cc.) In the experiment with Adams' catalyst, ferric chloride and succinic acid, the efficiency of the catalyst was proved by the addition of 0.5 g. of maleic acid; after 60 minutes, 125 cc. of hydrogen was absorbed and 0.25 g. of succinic acid was obtained by extraction with ether.

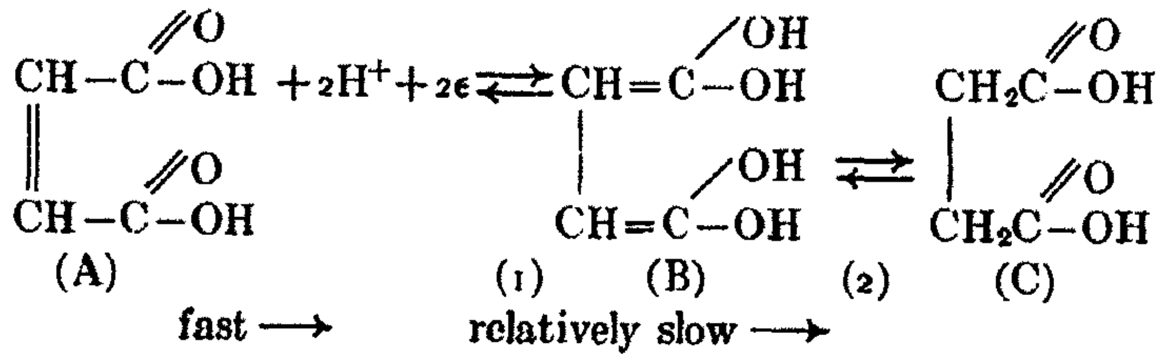
To recapitulate, if the process of catalytic hydrogenation (in solution at room temperature) is to be interpreted in the same terms as the process of reduction by soluble reducing agents, it must be assumed that the catalyst markedly changes the apparent reduction potential of the system. Experiments with a reducing agent almost as powerful as hydrogen show that this is not the case; the possibility of poisoning of the catalyst being excluded by experiment. The fact that the catalyst does not promote the oxidation of the reduced compound by an oxidizing agent of potential 0.8 volt above hydrogen clearly shows that the platinum is not a catalyst which has converted an irreversible system into a mobile reversible one. Our previous statement that "the process of catalytic hydrogenation can not be successfully formulated in terms of oxidation-reduction potentials" seems to represent accurately the facts and to place the process of catalytic hydrogenation in strong contrast to processes of irreversible reduction brought about by soluble reducing agents.

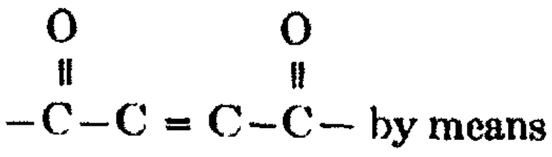
It is hardly necessary to add the qualification that we are discussing the catalytic hydrogenation of substances whose reduction products are *not* in mobile equilibrium with the oxidized form and a reducing agent. The action of hydrogen and platinum on substances of the first class enumerated at the beginning of this article, such as quinone, is, of course, a strictly reversible process and will proceed to an equilibrium point depending on the reduction potential of the organic system and the potential of the hydrogen electrode. The final position of equilibrium in such a mobile system must be in accord with an electrochemical formulation irrespective of whether the hydrogen-platinum combination acts in the same way as titanous chloride, for example, or in some entirely different manner. The mechanism of such relatively rare examples of catalytic hydrogenation can not be deduced, therefore, from electrochemical considerations.

The Mechanism of Irreversible Reduction and Catalytic Hydrogenation

The sharp contrast between the action of hydrogen and a platinum catalyst on maleic acid and the action of vanadous and chromous salts on the same substance points to a totally different mechanism for the two ways of irreversibly adding hydrogen atoms to the double linkage. Let us first consider, in some detail, the irreversible reduction of maleic acid and see if any reasonable mechanism can be suggested which would account for the observed facts. In the following discussion we shall make a number of more or less probable assumptions in regard to the numerical value of certain equilibrium constants and rates of reaction in order to outline a more definite picture than could be formulated in merely qualitative terms; we do not, of course, pretend that such an arbitrary procedure leads to any conclusions of quantitative significance but hope that it may suggest at least a possible explanation of the difference between reversible and irreversible systems. Lacking information in regard to the free energy change involved in the formation of succinic acid from maleic acid and hydrogen, we shall use the value 38 Cal. which is the total energy change from calorimetric measurements; this assumption that the total and free energy change are equal is probably not greatly in error.

It may be supposed that the action of a soluble reducing agent on maleic acid is similar to the reduction of quinone and that the first step is the addition of two hydrogen atoms to the oxygen atoms at the ends of the doubly conjugated system. This di-enol form of succinic acid (B in the equation below) would be very unstable and would rearrange to give succinic acid, and the mechanism of the reduction would be as shown below:



If it be assumed that the addition or removal of hydrogen atoms to compounds containing the system  $-\overset{\overset{O}{\|}}{C}-C=C-\overset{\overset{O}{\|}}{C}-$ by means of *soluble reducing* or *oxidizing agents* proceeds only through some intermediate compound such as the di-enol form (or its ions), the difference between quinone and maleic acid is readily explained. This difference is to be found in the fact that with hydroquinone the di-enol form is stable while with succinic acid it is highly unstable. In other words, the free energy of the first step of the scheme outlined above ($A \rightleftarrows B$) is practically equal to the free energy of the entire process in the case of quinone, while with maleic acid it is very much less than that of the total free energy change and may be of the opposite sign. For example, if the enolization constant[1] of a single enol group were 10^{-22}, the free energy of the change of the di-enol form of maleic acid to succinic acid (2 enol groups involved) would be $1.364 \times \log 10^{-44} = 60$ Cal. at 25°; in this case the free energy change of the system maleic acid, hydrogen, di-enol form of succinic acid, would be $38 - 60 = -22$ Cal. which corresponds to a potential (on the hydrogen scale) of -0.5 volt. Under such circumstances the action of a reducing agent of potential -0.30 in a solution normal with respect to hydrogen ions would cause the formation of only 10^{-7} moles of di-enol from 1 mol of maleic acid since the difference in potential between the reducing agent and the potential of the system (-0.5) is equal to $.0295 \log$ [di-enol] when the amount of di-enol formed is very small. The action of a more powerful reducing agent of potential -0.38 would form 10^{-4} mols. This equilibrium condition first attained would be continually upset by the rearrangement of the di-enol form into succinic acid, the concentration of the di-enol, however, would remain practically constant, more being very rapidly formed by the action of the reducing agent. The rate of this rearrangement and the amount of di-enol formed by the reducing agent in question would determine whether or not "appreciable reduction" occurred. Let us see how rapidly such ketonization would have to proceed in order to have 1% of the maleic acid reduced in 16 to 17 minutes (10^3 seconds) by a reducing agent of potential -0.30 volts on the one hand and a reducing agent of -0.38 volts potential on the other. If we start with one liter of molar maleic acid solution, this reduction corresponds to the formation of 10^{-2} moles in 1000 seconds or 10^{-5} moles per second; the di-enol form must rearrange at this rate which will be practically uniform since this is a rather unusual instance of a monomolecular reaction fed by a much more rapid reversible reaction. With the reducing agent of potential -0.30, the amount of di-enol in equilibrium is only 10^{-7} moles and in order for 10^{-5} moles of this to rearrange each second it is obvious that the rate of this monomolecular isomerization must be such that one-half of the equilibrium amount (0.5×10^{-7}) will rearrange in 5×10^{-3} seconds. On the other hand, with a reagent of potential -0.38 since there are 10^{-4} moles in equilibrium the rate of rearrangement would only have to be such that half the material ketonized in 5 seconds. The actual rate of ketonization of the

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[1] The value 10^{-22} for the enolization has been assumed quite arbitrarily in order to demonstrate the influence of this factor. Some such very small value probably is somewhere near the truth since the α hydrogen atom in acids is much less active than in ketones where the value is too small to be measured.

enol form of acetoacetic ester as measured by Meyer[1] in aqueous solution corresponds to half isomerization in 6 seconds. However, as this rate would undoubtedly be faster in the presence of acids, not too much significance can be attached to a comparison between it and the rates just calculated, but it indicates the order of magnitude of such speeds of ketonization as have been observed.

Since the ratio of the speeds of the enolization and ketonization are equal to the equilibrium constant of the change from succinic acid to the di-enol form which we have assumed to be very small, one can postulate either a very high speed of ketonization or a very low speed of enolization. We are inclined to believe that the magnitude of the rate of ketonization is not very different from that observed with such substances as acetoacetic ester and that the rate of enolization is correspondingly small. This would account for the fact that oxidizing agents which readily oxidize hydroquinones are without appreciable effect on succinic acid, for if these oxidizing agents are only effective in removing hydrogen atoms from enolic and phenolic substances the process could proceed no faster than this very slow enolization. If $k_1/k_2 = 10^{-44}$ and k_2 corresponded to the ketonization rates given above, it is evident that any process that must proceed through the enol form would not be appreciable in a life time. Thus, if one merely assumes that soluble oxidizing and reducing agents of the type of ferric chloride and chromous chloride can not directly remove or add hydrogen atoms to the carbon linkage but only to the oxygen atoms at the ends of the doubly conjugated system, one arrives at a satisfactory explanation of the reversible reduction of quinones on the one hand and the irreversible reduction of maleic acid on the other. The fact that no case appears to be on record of the reduction of an ethylene hydrocarbon by a soluble reducing agent is in harmony with the assumption underlying the mechanism just proposed. It is true that acetylene is reduced to ethylene by chromous chloride but this may be due to peculiarities inherent in the triple linkage.

Ethylene hydrocarbons are readily hydrogenated catalytically and there is every reason to believe that the hydrogenation of the double linkage in maleic acid proceeds in a similar manner. From our point of view, the catalyst activates the gaseous hydrogen and adds hydrogen atoms directly to the ethylene linkage in contrast to chromous chloride which adds hydrogen only to the oxygen atoms at the end of the conjugated system. From the difference in the two mechanisms arise the differences between irreversible reduction and catalytic hydrogenation which we have considered in this and our earlier paper.

If one now seeks for the reason why soluble reducing agents and oxidizing agents are only effective in their action on organic substances containing certain linkages, the answer must be found in the mechanism underlying the oxidation and reduction of these reagents themselves. While the electrochemical equations for reversible oxidation and reduction can be derived

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[1] Ann. 380, 235 (1911).

either from the concept of hydrogen in equilibrium with the reagents or in terms of electron transfer, the most satisfactory picture of these reversible changes seem to be arrived at from the latter point of view. The tremendously small hydrogen pressures which must be postulated and the fact that satisfactory oxidation-reduction potentials can be measured with electrodes[1] which will not function as hydrogen electrodes, are arguments against the concept of an oxidation-reduction electrode as a low pressure hydrogen electrode. The fact that satisfactory potentials of mixtures of ferrous and ferric salts can be measured in anhydrous pyridin[2] seems convincing proof that a direct interchange of electrons between the ions is the essential feature of many cases of oxidation and reduction in inorganic chemistry. If the action of chromous chloride[3] on ferric chloride, for example, is thus merely the transfer of an electron from the chromous to the ferric ion, there is every reason to believe that a similar mechanism takes place when chromous chloride reduces an organic compound. In the cases which we are considering, however,the resulting negatively-charged organic molecule can not exist by itself in aqueous acid solution but combines with hydrogen ions and becomes an electrically neutral molecule. It is an interesting problem whether this addition of two electrons and two hydrogen ions takes place in the order just mentioned or in the reverse order or simultaneously; no evidence appears now available which would enable one to distinguish between these three possibilities. The change may be represented as:

$$A + 2\epsilon + 2H^+ \rightleftharpoons AH_2$$

From our point of view, the reduction of an organic compound in homogeneous solution, whether reversible or irreversible, is primarily a process of electron transfer usually accompanied by the capture of hydrogen ions by the organic molecule.[4] It is very tempting to speculate as to why this electron transfer takes place with certain types of compounds and not with others but until we have completed our study of the reversible and irreversible reduction of a wide variety of substances, we prefer not to hazard an explanation of this fundamental question. There has been a tendency in recent years to represent all processes of oxidation and reduction as essentially electronic but this seems to us a rash and unwise generalization which greatly endangers the fruitfulness of the modern electrochemical conception of oxidation and reduction. As we have attempted to bring out in this discussion of irreversible reduction and catalytic hydrogenation, there are certain processes involving the gain or loss of hydrogen atoms (or their equivalents) which can be successfully formulated in terms of electron transfer and at least one other which

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[1] L. P. Hammett: J. Am. Chem. Soc. 46, 7 (1924).

[2] Z. Elektrochem. 15, 264 (1909).

[3] F. Foerster: "Elektrochemie wässeriger Lösungen," pp. 211-212.

[4] As pointed out in another paper from this Laboratory (J. Am. Chem. Soc. 44, 2480 (1922) in certain cases of reversible reduction where the reduced compound forms a disodium salt, the actual reduction product formed in alkaline solution is a negatively charged ion; no hydrogen is apparantly involved in the reduction. However, since this represents a final equilibrium condition, no conclusions can be drawn from such facts in regard to the mechanism by which this equilibrium is reached.

can not. Whether any given process is to be formulated in electrochemical terms is a problem to be settled by experiment and not by purely theoretical argument.

In this paper we have confined out attention to the irreversible reduction of one particular type of substance in order to examine the difference between this process and catalytic hydrogenation. An extension of this general point of view to other types of irreversible reduction and also to cases of irreversible oxidation will be reserved for a later paper. The number of examples of such irreversible processes of reduction and oxidation is very great not only in organic but also in inorganic chemistry. The familiar fact that sulfurous acid or sulfites may be oxidized to sulfuric acid or sulfates but that these can not be reduced in aqueous solution is a striking example of an irreversible oxidation. It should be possible to characterize such processes by determining their "apparent oxidation potential" much as we have measured the apparent reduction potential of a variety of organic compounds, and we are now examining the oxidation of aminophenols, and benzoin from this point of view. If our electrochemical interpretation of such irrevresible reductions and oxidations is correct, there must, in every instance, be a relatively fast reaction involving electron transfer followed by an essentially irreversible process leading to the final product. In reversible processes the oxidized form can rapidly give up electrons and the reduced form rapidly acquire them whereas in the cases of irreversible oxidation or reduction only one of these steps takes place at an appreciable rate. A more precise formulation of the mechanism of each type of irreversible oxidation or reduction must await further experimentation.

THE JOULE-THOMSON EFFECT FOR HELIUM[*]

BY JOHN H. PERRY

The purpose of this paper is to give the results of some calculations of the Joule-Thomson coefficients of helium. These computations are based upon an equation of state of the Keyes type.[1]

This form of the equation of state has been tested by comparing the delta term (which corresponds to van der Waals "b"), and the cohesive pressure term $A/(V+l)^2$ (which corresponds to van der Waals (A/v^2), separately at high pressures and a considerable range of temperature. This type of equation of state has been tested very carefully by physical mensurements for a considerable number of substances by Dr. F. G. Keyes and co-workers, with very good success.

In order to give a survey of the degree of exactness with which this tentative equation of state for helium accords with measurements, there is presented in the following tables, a comparison of calculated values with the data observed by: Table I, H. Kammerlingh Onnes, (2) Proc. Koninklijke Akademie van Wetenschappen Amsterdam, Vol. **10**, page 445; Table II, Holborn and Schultze: Ann. Physik., Vol. **47**, page 1110; and Table III, Holburn and Otto; Zeit. physik., **10**; page 372.

The Keyes type of equation of state: $P=\dfrac{RT}{V-\delta}-\dfrac{A}{(V+l)^2}$ has been discussed considerably in the literature.[2] Further discussion in this paper would be superfluous. Let it be sufficient to emphasize here that in the case of a polyatomic substance delta is an inverse function of the volume, but for monatomic molecules delta is a constant.

The equation of state[3] for helium is:

$$P=\frac{20.53}{V-3.17}-\frac{3285}{(V+6.85)^2}$$

The dimensions of the quantities involved in this equation will, in this paper, be:

P = pressure, in atmospheres of 76 cm. of mercury

v = volume, in cubic centimeters per gram.

T = absolute temperature on the centigrade scale; the ice point is taken to be 273.14 degrees Kelvin.

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[*] Published by permission of the Director, U. S. Bureau of Mines.

[1] Keyes: Proc. Nat. Acad. Sci. 3, 323 (1917); Keyes and Felsing: J. Am. Chem Soc. **41**, 589 (1919); Keyes: J. Am. Chem. Soc. **42**, 54 (1920); Phillips: J. Math. and Phys. Mass. Inst. Tech. **1**, 42 (1921); Proc. Nat. Acad. Sci., **7**, 172 (1921); Keyes: J. Am.. Chem. Soc. **43**, 1452 (1921); Keyes, Smith and Joubert; J. Math. and Phys. Mass. Inst-Tech. **1**, 95 (1922); Taylor and Smith: J. Am. Chem. Soc., **45**, 2108 (1923).

[2] Keyes: loc. cit.

[3] Private communication from Dr. F. G. Keyes.

TABLE I

T °C	T °K	Volume cc/gm.	Pressure (atms) Calc'd	Pressure (atms) Observed
+100.35	373.49	182.608	42.640	42.574
		143.362	54.549	54.459
		117.763	66.702	66.590
+ 20.00	293.14	221.130	27.548	27.539
		168.308	36.336	36.303
		114.694	53.741	53.708
00.00	273.14	213.343	26.613	26.634
		148.007	38.590	38.565
		114.360	50.209	50.240
−103.57	169.57	171.923	20.527	20.580
		147.387	24.001	24.100
		122.120	29.069	29.185
		107.179	33.218	33.383
−182.75	90.39	137.697	13.637	13.751
		118.590	15.869	16.019
		104.833	17.990	18.169
−216.56	56.58	123.826	9.445	9.564
		112.975	10.350	10.502
		104.473	11.201	11.448

TABLE II

T°C	T°K	Vol cc/gm	Pressure Observed	Pressure Calc'd equation of state
100	373.14	156.499	49.830	49.838
100	373.14	156.721	49.759	49.766
100	373.14	390.665	19.745	19.748
100	373.14	392.683	19.643	19.646
50	323.14	144.699	46.7316	46.731
50	323.14	145.967	46.326	46.317
50	323.14	264.872	25.305	25.305
50	323.14	265.973	25.207	25.199
0	273.14	114.100	50.432	50.325
0	273.14	115.680	49.729	49.622
0	273.14	224.013	25.363	25.330
0	273.14	224.563	25.301	25.267

Table III

T		Volume	Pressure (atms)	
°C	°K	cc/gm	Observed	Calc'd eq. of state
0	273.14	4263.6	1.315	1.316
0	273.14	429.003	13.157	13.151
0	273.14	215.994	26.315	26.282
0	273.14	144.962	39.473	39.405
0	273.14	109.468	52.631	52.510
0	273.14	86.171	65.782	65.608
0	273.14	73.974	78.947	78.696
0	273.14	63.826	92.105	91.791
0	273.14	56.221	105.263	104.875
50	323.14	5043.41	1.315	1.316
50	323.14	506.985	13.157	13.155
50	323.14	254.963	26.315	26.299
50	323.14	170.956	39.473	39.435
50	323.14	128.942	52.631	52.568
50	323.14	103.742	65.789	65.695
50	323.14	86.942	78.947	78.818
50	323.14	74.942	92.105	91.941
50	323.14	65.942	105.263	105.065
100	373.14	5823.225	1.315	1.316
100	373.14	584.923	13.157	13.158
100	373.14	293.890	26.315	26.314
100	373.14	196.744	39.473	39.495
100	373.14	148.395	52.631	52.613
100	373.14	119.287	65.789	65.766
100	373.14	99.845	78.947	78.951
100	373.14	86.027	92.105	92.074
100	373.14	75.636	105.263	105.229

Having shown that the calculated and observed values for helium are comparable over a considerable range of pressure and temperature, it has been found interesting to calculate the Joule-Kelvin coefficients.

The Joule-Kelvin effect can be readily derived if we consider a given mass of gas in its first condition and in its final condition. The condition under which this effect is taking place is that the change in the function (U+pv) should be zero, i.e., d (U+pv)=O. We can write (u+pv) as a function of pressure and temperature and we then obtain:

$$\delta(U+pv)=O=\left[\frac{\delta(U+pv)}{\delta T}\right]_p dT+\left[\frac{\delta(U+pv)}{\delta p}\right]_T dp$$

$$\text{or}\left(\frac{dU+pdv}{dT}\right)_p dT=-\left(\frac{dU+pdv+vdp}{dp}\right)_T dp$$

$$\mathrm{Cp\,dT} = -\left(\left(\frac{du}{\delta p}\right)_T + V + P\left(\frac{\delta v}{\delta p}\right)_T\right)dp$$

but $\left(\frac{\delta u}{\delta p}\right)_T = -P\left(\frac{\delta v}{\delta p}\right)_T - T\left(\frac{\delta v}{\delta T}\right)_p$

$$\therefore \mathrm{Cp\,dT} = -\left(V - T\left(\frac{\delta v}{\delta T}\right)_p\right)dp$$

Cancelling and collecting terms:

$$\mu = \left(\frac{\delta T}{\delta p}\right)_H = \frac{T\left(\frac{\delta v}{\delta T}\right)_p - V}{\mathrm{Cp}}$$

where H is the function (U+pv) and μ is the Joule-Thomson coefficient.

The value of the differential $\left(\frac{\delta v}{\delta T}\right)_p$ becomes, from the equation of state:

$$\left(\frac{\delta v}{\delta T}\right)_p = \frac{R/v-\delta}{\frac{RT}{(v-\delta)^2} - \frac{2A}{(v+l)^3}}$$

which becomes for helium: $= \frac{\frac{20.53}{v-3.17}}{\frac{20.53T}{(v-3.17)^2} - \frac{6570}{(v+6.85)^3}}$

and the value of μ, the Joule-Thomson coefficient becomes equal to:

$$\mu = \frac{\frac{\frac{20.53}{v-3.17}T}{\frac{20.53T}{(v-3.17)^2} - \frac{6570}{(v+6.85)^3}} - V}{\mathrm{Cp}}$$

The value for the specific heat at constant pressure has been taken as 1.2662 calories per gram per degree, from the results of Eucken[1] and Eggert[2].. This value of the specific heat when converted into the proper units, is equal to 52.2814 cc-atmospheres per degree per gram.

The equation of state for helium begins to deviate from the observed values below 25 degrees Kelvin and for that reason the values for μ at that temperature have not been included.

The following, Table II, gives a résumé of the calculations:

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[1] Eucken: Verh. deutsch. physik. Ges. 18, pp. 8-9 (1916).

[2] Eggert: Ann. physik. 44, 643-56.

TABLE II

T °Kelvin	μ Pressure (atms)				
	1	5	25	50	100
50	+.059	+.0482	+.0065	−.0226	
75	+.0188	+.0144	−.0069	−.0245	
100	−.0003	−.0033	−.0163	−.0280	−.0418
150	−.0203	−.0216	−.0280	−.0342	−.0428
200	−.0304	−.0313	−.0348	−.0387	−.0445
300	−.0446	−.0407	−.0419	−.0444	−.0475

The inversion temperature is defined as that temperature at which the Joule-Thomson effect changes sign, that is, where μ is equal to zero. The inversion temperature for helium at one atmosphere is very slightly below 100° Kelvin. As is evident from an inspection of the data above, the inversion temperature decreases as the pressure increases.

Summary

1. An equation of state, of the Keyes type, for helium is used in comparing calculated values with the observed data from three different sources. Very good agreement is obtained throughout a temperature range of 50°K to 375°K and for pressures up to 105 atmospheres.

2. Joule-Thomson coefficients for the five isobars: 1—5—25—50—100 atmospheres have been calculated. The inversion temperature for helium at one atmosphere has been determined to be slightly less than 100°K.

THE IONIZATION OF STRONG ELECTROLYTES*

BY WORTH H. RODEBUSH

In a recent paper[1] the condition of highly polar substances in solution was discussed, and it was pointed out that this condition was in general quite different from the state which has usually been pictured for a salt that is completely ionized. It was predicted that the greatest departure from a state where the ions are actually free would be found at concentrations in the neighborhood of molal. This prediction has received a striking confirmation in the work of Lewis and Randall[2] who have found a minimum to exist in the activity of the strong electrolytes in the neighborhood of molal concentrations, and that the activity coefficient rises to very high values in concentrated solutions.

The case of the very dilute solution still offers an opportunity for some very interesting observations. It is probable that no such thing as a completely polar electrolyte exists just as there are no perfect gases, but helium is very nearly a perfect gas and potassium chlorid must be very nearly a completely polar substance, and as in the case of the gas laws, we shall find it profitable to discuss the ideal case.

A completely polar salt when in dilute solution would then be completely ionized in the sense that none or comparatively few of the positive and negative ions would be joined together in the position and orientation of the crystal lattice. That molecules of sodium chlorid exist in solution in a manner analogous to molecules in sodium chlorid vapor seems very doubtful. Recent calculations by Latimer[3] show that a molecule of sodium chlorid in the vapor state is much more likely to dissociate into sodium and chlorine atoms than it is into the ions. The case is certainly far different in solution and analogies between solution and vapor are rather far fetched.

It has been generally recognized that ions are hydrated in solution but it has not been recognized to what an extent this must be true. There is no reason to suppose that a salt like potassium chlorid would dissolve at all were it not that the water molecules possess the power of neutralizing the electrical fields surrounding the potassium and chlorine ions. It seems probable that all ions are surrounded in solution by an envelope of water molecules. In the case of the chlorine ion with a negative charge and an outer shell of negative electrons the water molecules would be oriented with the hydrogens attached to the chlorine. In the case of the potassium ion the positive charge of the ion would counteract the negative external electron shell and the orientation of the water molecules would be problematical. Certainly they would be

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*Contribution from the Chemical Laboratory of the University of Illinois.

[1] Latimer and Rodebush: J. Am. Chem. Soc. **42**, 1419 (1920).

[2] Lewis and Randall: J. Am. Chem. Soc. **43**, 1125, (1921).

[3] Latimer: J. Am. Chem. Soc. 45, 2803 (1923).

held more loosely and this agrees with the common conception that potassium is one of the least hydrated ions. This solvation of the ions would tend to cause a positive deviation from Raoult's law since the amount of free solvent would be actually less than the calculated amount. At 0.01 molal this effect would be negligible and since the ions are enveloped in water molecules, the solute now resembles the solvent and we have a condition where we should expect Raoult's law to hold were it not for the electrical forces. These are far from negligible. In a 0.01 molal solution of potassium chlorid on the assumption of regular distribution the average distance between ions is of the order 10^{-6} cms. The force exerted by one ion upon another at this distance is given by Coulombs law

$$f = \frac{e_1 e_2}{kr^2} = 10^{-9} \text{ dynes}$$

which is about the same force as would be exerted by a potential drop of 600 volts per cm. in vacuo. The applied potential is obviously not likely to affect the degree of ionization of an electrolyte appreciably.

Since a system tends to take on a configuration of minimum potential energy the ions will not be arranged in a regular distribution but there will be a tendency for ions of unlike sign to approach each other. Opposed to this will be the effect of the thermal agitation of the molecules.

The problem of the distribution of the ions in a dilute solution is therefore a statistical one and attempts have been made by a number of investigators to solve it. Milner[1] approached the problem from a rigorous mathematical basis but he was not able to obtain a complete and satisfactory solution. The chief fault in Ghosh's work[2] was his failure to postulate a consistent clear picture of the actual distribution of the ions in solution. The first apparently successful attempt in this direction has been made by Debye[3] who, by a straight forward application of the theory of electrostatic potential together with the Maxwell-Boltzman distribution law, has arrived at an expression for the free energy of a completely polar electrolyte in solution. Debye has derived a general expression for solutions of any concentration but the effective diameters of the ions enter into the expression in all except very dilute solutions where the diameter of the ions may be neglected. Since we have no data for the effective diameter of any ion, we can only hope to verify Debye's expression in dilute solution. The expression obtained by Debye for the partial molal free energy of a completely polar electrolyte in dilute solution is

$$\bar{F}_s = \Sigma \upsilon_i \, RT \ln m - \frac{\Sigma (\upsilon_i z_i^2)^{3/2} N_o^{3/2} \epsilon^3 (4\pi)^{1/2} m^{1/2}}{3\, D^{3/2} (kT)^{1/2} V_o^{1/2}} + C \quad (1)$$

Here m is the stoichometric molality, N_o is Avogadro's number, ϵ is the charge of the electron, D is the dielectric constant of the solvent, V_o is the volume of the solution, (1000 cc) C is a constant and kT has its usual significance. $\Sigma \upsilon_i$; is the number of ions per molecule and $\Sigma \upsilon_i z_i^2$ is the sum of the products

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[1] Milner: Phil. Mag. 25, 742 (1913).

[2] Ghosh: J. Chem. Soc., 113, 790 (1918).

[3] Debye and Hückel: Physik. Z. 24, 185 (1923).

of the number of each kind of ion per molecule multiplied by the square of its charge, and is directly proportional to the quantity Lewis has termed the ionic strength.

The second term in the equation above would give the free energy of an ideal solute and the third term shows that the free energy of an electrolyte in dilute solution is always less than that for an ideal solute. It is seen that even in the most dilute solution that we can study, the attraction between ions causes a negative deviation from Raoult's law.

While it appears doubtful if Debye's calculations can give us a very exact account of irreversible phenomena such as conductivity, they should be capable of withstanding a rigorous check against activity measurements in dilute solution. On account of the errors entering into activity measurements in dilute solution we can not put too much dependence in the data for any individual salt. Fortunately we do not need to. G. N. Lewis with Linhart and Randall has obtained from a careful scrutiny of all available data, two empirical generalizations regarding the activity of strong electrolytes in dilute solution. If we can derive these empirical rules from Debye's theory then we shall have the most rigorous experimental check of Debye's theory possible.

The first of these rules is the freezing point law of Lewis and Linhart[1] which may be written

$$\frac{\Theta}{1.86\Sigma\upsilon_i m} = 1 - \beta m^{\alpha} \tag{2}$$

Here Θ is the actual freezing point lowering of a solution of molality m, and α and β are constants.

Let us see to what form of freezing point equation the Debye expression will lead.

From thermodynamics we have the fundamental equation for aqueous solutions.

$$\frac{\delta\Theta}{\delta m} = \frac{mT}{55.5\Delta H}\left(\frac{\delta\bar{F}_s}{\delta m}\right) \tag{3}$$

Substituting the value from (1) of $\frac{\delta\bar{F}_s}{\delta m}$

$$\frac{\delta\Theta}{\delta m} = \frac{mT}{55.5\Delta H_f}\left[\frac{\Sigma\upsilon_i RT}{m} - \Sigma\frac{(\upsilon_i z_i^2)^{3/2}\epsilon^3 N_o^{3/2}(4\pi)^{1/2} m^{-1/2}}{6\ D^{3/2}(kT)^{1/2} V_o^{1/2}}\right] \tag{4}$$

Integrating with respect to $\alpha\Theta$ and αm and rearranging, we have for very dilute solutions

$$\frac{\Theta}{1.86\Sigma\upsilon_i m} = 1 - \frac{\Sigma\,(\upsilon_i z_i^2)^{3/2}\ N_o^2\epsilon^3(4\pi)^{1/2}\,m^{1/2}}{9\,\Sigma\upsilon_i\ \ (DRT)^{3/2}\ V_o^{1/2}} \tag{5}$$

or

$$\frac{\Theta}{186\Sigma\upsilon_i\,m} = 1 - \beta m^{1/2}$$

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[1] Lewis and Linhart: J. Am. Chem. Soc. 41, 1951 (1919).

This is exactly the Lewis-Linhart equation. It remains to compare the values of the constants. The value for α from the Debye expression is, of course, ½ for all types of electrolytes. Upon substituting the values of the constants in the last term of equation (5) we obtain[1]

$$\beta = 0.205 \frac{\Sigma(\upsilon_i z_i^2)^{3/2}}{\Sigma\upsilon_i} \tag{7}$$

as the general expression for β. For uni-univalent electrolytes, we obtain

$$\beta = 0.290 \quad \alpha = 0.500$$

While Lewis and Randall obtained for potassium and sodium chlorides

$$\beta = 0.329 \quad \alpha = 0.535$$

For other types of electrolytes, we have the following comparison.

	Calculated		Experimental	
	β	α	β	α
uni-bivalent	1.00	0.500	0.572	0.374
Bi-bivalent	2.32	0.500	1.44	0.38

In the case of the uni-univalent salts where the data are most accurate the agreement is most satisfactory. In the case of the other types of salts the freezing point data in dilute solution are so uncertain that no better agreement is to be expected.

The second empirical rule of Lewis and Randall relates to activity coefficients as obtained from solubility data in mixed electrolytes. It amounts to a more exact statement of the relation which was vaguely formulated as the isohydric principle. It is as follows: In dilute solutions the activity coefficient of a given electrolyte is the same in all solutions of the same ionic strength[2]. The application of Equation (1) to activity of a slightly soluble salt in the presence of other electrolytes requires a careful consideration of the way in which (1) depends (a) upon the concentration of the ions of the slightly soluble salt, (b) upon the total ion concentration. Inspection of the derivation of (1) shows that it may be written in the form

$$\bar{F}_s = \Sigma\upsilon_i \text{ RT ln m} + \beta\, \Sigma\, (\upsilon_i z_i^2)^{1/2}\, m^{1/2} + C \tag{8}$$

where $\Sigma(\upsilon_i z_i^2)^{1/2} m^{1/2}$ refers to the total ion concentration. The remainder of the constants of the third term of (1) were represented by β. The value of β will therefore vary when the valence type of the slightly soluble salt varies since it contains the term $\Sigma(\upsilon_i z_i^2)$ Since $\bar{F}_s$ must be equal to the free energy of the solid salt C will be different for different salts. Salts whose ions are able to combine in crystal lattice in such a way as to neutralize effectively their electrical fields will be slightly soluble. The solubility of highly polar salts thus depends largely on what Born has called the grating energy.

If we write

$$\bar{F}_s = \Sigma\upsilon_i \text{ RT ln } \alpha$$

where α is the mean activity of the ions of the slightly soluble salt then (8) may be transformed into the following equation

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[1] The value used for D is 80. For pure water it is usually taken as 87.

[2] Lewis and Randall: J. Am. Chem. Soc. 43, 1141 (1921).

$$\ln \frac{\alpha}{m} = \beta_1 \Sigma(\nu_i z_i^2)^{1/2} m^{1/2} + C_1 \qquad (9)$$

Here $\frac{\alpha}{m}$ is the mean activity coefficient and $\frac{\Sigma(\nu_i z_i^2)m}{2}$ is the ionic strength as defined by Lewis. The above equation shows that a linear relation exists between the logarithm of the activity coefficient and the square root of the ionic strength in dilute solutions. This relation was shown by Lewis to hold for such data as are available[1].

The foregoing results justify the prediction that the equation of Debye for the free energy of strong electrolytes will be found to hold with great exactness for all types of strong electrolytes in dilute solution. In order to obtain further verification, it is necessary that more exact data be obtained for activities in dilute solution. Work along this line is in progress in this laboratory.

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[1] Actually Lewis plotted α/m instead of $\ln \alpha/m$ but the above conclusion holds as may be readily seen by replotting Lewis' data.

Urbana, Illinois.

NEW BOOKS

A Dictionary of Applied Chemistry. *By Sir Edward Thorpe. Vol. V.* 23 × 16 *cm; pp. viii* + *722. New York: Longmans, Green and Co., 1923. Price: $20.00.* The fifth volume includes such topics as oxygen, ozone, paint, palladium, paper, paraffin, parchment, pearls, perfumes, petroleum, phenacetine, phenanthrene, phenol, phosphorus, photography, photosynthesis, phthalic acid, picric acid, pigments, pitch, plant-sprays, platinum, polarimetry, potassium, pottery, precipitation (electrical), primuline, propyl, proteins, pyrazolone, pyrimidines, pyrometry, pyrotechny, quartz, quinoline, quinones, racemism, radiology, radium, refractometer, refractories, refrigerating and ice-making machinery, resins, rhodium, rubber, rum, and ruthenium.

Under the cracking of petroleum, p. 148, there is the statement that "there is some doubt as to the reasons for granting a patent for the Burton process, because the operations are precisely similar to those patented by Dewar and Redwood in 1889; viz, the distillation and condensation were carried out under pressure. It is true that these operations were devised to produce larger yields of kerosene, that product being much more important than motor spirit at the period of the granting of the original patent; but the apparatus devised by Dewar and Redwood would give results similar to those which are being obtained with the Burton process."

The reviewer was especially interested at this time in the articles on photography by Gamble and on photosynthesis by Baly and Heilbron. One regrets to see, however, the statement, p. 207, that "the sensitiveness, or to speak from a practical point of view, the 'speed', which is not the same thing, of the modern dry plate is something which has only been attained by long and careful experiment under the conditions of manufacture on a working scale, for there is something about the dry plate which seems to defy mere laboratory elucidation alone, using the term to denote manufacture on a small scale." All that means is that the people who have developed the dry-plate industry are so hopelessly empirical that they cannot find out what they do or why they do it even when they are actually doing it right along on a commercial scale.

It is interesting to note, p. 227, that "in the development of aerial negatives during the recent war, the printing quality was largely determined by the regulated stain image (non-sulphited pyro-metol developer)." There is practically nothing as to the theory of the action of color sensitizing, p. 227. It is postulated quite definitely, p. 238, that the developer reacts only with dissolved silver bromide.

"When the reducer diffuses into the emulsion film and reaches the halide grain the silver salt passes into solution and is ionised; reaction then occurs between the ion [?] or the reducer and the silver ion. The latter loses its charge, producing silver in solution, which solution soon becomes saturated and equilibrium is attained [?]. In the presence of a nucleus on which the silver can be precipitated, this equilibrium is not maintained, and the action proceeds until the grain is wholly reduced. The difference between unexposed and exposed silver halide is shown by the fact that one will develop and the other will not. The action of light, whatever it may be, is to produce that difference, the nucleus which will provide the deposition centre in the grain for precipitated silver."

Nobody would guess from that passage that it is possible to develop a positive direct by using a different developer. We have here a striking instance of the way in which people come to grief because they do not take the trouble to consider the whole of the subject.

When discussing photosynthesis Baly and Heilbron point out, p. 260, that there are three stages in any reaction. In the first stage the molecule is brought into a reactive state by the supply of a definite amount of energy, which must always be exactly one or more of its molecular quanta. The second stage is the atomic re-arrangement, whereby new molecules are produced. In the third and final stage the molecule passes into its normal and non-reactive state.

"This deduction from the energy quantum theory and the recognition of the three stages of any reaction is of supreme importance, since it correlates all reactions and shows that in order to induce any reaction it is first of all necessary to supply energy to the system so as to activate the molecules, this being true however exothermic the reaction may be. There are three methods by which the energy necessary for the first stage may be supplied. It may be supplied by a material catalyst, or as radiant energy either in the form of heat or light. The action of a catalyst does not arise here, and need only be mentioned in order to guard against any misconception. Many reactions take place in solution without the apparent intervention of the first stage, but in such cases the molecules have been activated by the solvent which functions as a catalyst. In general it is a matter of little consequence whether a molecule is activated by heat or light, that is by infra-red or ultra-violet rays, in view of the known integral relationships that exist between the frequencies at which a molecule can absorb energy. It is a matter of cardinal importance, however, in the case of highly endothermic reactions, in which the increment of energy necessary for the initial phase change must obviously be a large number of molecular quanta. When a molecule absorbs energy at its principal frequency in the infra-red it absorbs it in terms of its molecular quantum, but if it absorbs ultraviolet light the unit of energy absorbed is a quantum which is an integral multiple of the molecular quantum, the multiple depending on the phase in which the molecule exists. One single quantum of energy absorbed at the characteristic frequency in the ultra-violet is always sufficient to activate a single molecule for any reaction however endothermic this may be."

The conclusion drawn by Moore and Webster that "iron salts play a more important rôle in the plant than chlorophyll is quite unsound as Willstätter has clearly proved. The effect of chlorosis caused in the leaves when the plant is starved of iron salts is most probably to be explained by the fact that they aid the synthesis of pyrrole which enters so largely into the constitution of chlorophyll. This is exactly analogous to the therapeutic value of iron in cases of anaemia in man, haemoglobin and chlorophyll having been shown by Willstätter to be similar in their constitution," p. 262.

"It has been shown by experiments carried out in Liverpool that the necessary wave-length of the light [which causes polymerisation of formaldehyde to reducing sugars] is 290 $\mu\mu$, which at once establishes the fact that the polymerisation of the formaldehyde is photochemically distinct from its synthesis [which is caused by a wave-length of 200 $\mu\mu$]. The importance of this observation lies in the conclusion that if ordinary formaldehyde were produced in the plant it would be necessary to consider the mechanism of its photocatalytic activation. Although it has been proved that the polymerisation of formaldehyde can be photolysed, this is of scientific interest only, because there is no need to postulate such a mechanism in the plant. On exposure to light of wave-length 290 $\mu\mu$, the formaldehyde molecules absorb energy quanta and are converted into an active phase of high energy content, and it is these molecules which at once undergo polymerisation to sugars, it being well known that formaldehyde in its ordinary form does not polymerise in this way. It has further been proved, and this is a fact of fundamental importance, that the formaldehyde molecules when first produced by photosynthesis exist in the same reactive phase as when they are photochemically activated by the action of light of wave-length 290 $\mu\mu$ on ordinary formaldehyde. Since the photochemically activated molecules polymerise to sugars, the freshly photosynthesized molecules do the same. This not only explains the absence of ordinary formaldehyde in the growing leaf, but it also eliminates the serious difficulty which would otherwise arise, namely, the necessity of the photocatalytic activation of the ordinary formaldehyde, if such were produced, as a separate step in the process whereby sugars are synthesised in the plant," p. 262.

Baly and Heilbron say, p. 265, that "there is no doubt that formhydroxamic acid marks the first step in the phytosynthesis of the nitrogen compounds found in the plant. This has been proved, not only by the fact that this compound is actually produced by the direct action of activated formaldehyde on potassium nitrite, but also by the fact that activated formhydroxamic acid reacts with activated formaldehyde to give compounds which are known to occur in the living plant."

Wilder D. Bancroft

Practical Bacteriology for Chemical Students. *By Edward Ellis. 19 × 13 cm; pp. viii + 136. London and New York: Longmans, Green and Co., 1923. Price: $1.50.* The book is essentially a series of exercises designed to acquaint the student with bacteriological methods and technic. About six common bacteria, a yeast, and eleven species or genera of moulds are partially described. Methods for the examination of water and sewage are given.

It is difficult to see how sugar media prepared according to the author's technic can be expected to remain sterile. No mention is made of present day methods for the adjustment of the reaction of culture media to definite hydrogen ion concentrations. The methods for the examination of water and sewage differ greatly from those used by American bacteriologists. No serious attempt is made to present a classification of bacteria, yeasts, or moulds and no references are given to more comprehensive works. Figures 36 and 37 are missing.

A chemist confronted with problems involving bacteriology would obtain little help from this book, except some information on bacteriological technic that might be obtained from anyone of a large number of standard works. *F. R. Georgia*

A Course of Laboratory Experiments on Physico-Chemical Principles. *By Miles S. Sherrill. 22 × 15 cm; pp. xi + 125. New York: The Macmillan Co., 1923. Price: $7.00.* In the preface the author says: "This book presents a group of laboratory experiments which have been developed during a period of many years at the Massachusetts Institute of Technology as part of the general course of instruction in Chemical Principles given to junior and senior students in Chemistry and Chemical Engineering. Although especially designed to supplement Noyes and Sherrill's "Chemical Principles," . . . the experiments are presented in a form suited to accompany any text-book of physical chemistry.

"The main purpose of this laboratory course is to illustrate and to emphasize the principles that are being simultaneously considered in the class-room, by giving the student a more concrete acquaintance with the underlying phenomena. It serves also to illustrate some of the common methods of physico-chemical measurement. If differs, however, from most previous laboratory manuals of physical chemistry in the respect that this is an incidental, not a primary feature; emphasis being here placed on illustrating fundamental principles in close coördination with the general class-room course on the subject."

The chapters are entitled: molecular weight from vapor-density; vapor-pressure and its lowering by solutes; distillation in relation to vapor-pressure; distribution of solutes between phases; freezing-point lowering and molal composition; electrolysis, transference, and conductance; rate of chemical change; the equilibrium of chemical changes at constant temperature: equilibrium of chemical systems in relation to the phases present: heat effects attending chemical change; electromotive force of cells; effect of temperature on chemical equilibrium.

This book contains twenty-seven carefully chosen experiments, for each of which explicit directions are given. The exercises are necessarily rather formal, but the reviewer, notwithstanding, was especially pleased with the experiments on homogeneous and heterogeneous chemical equilibrium involving the dissociation of hydrogen iodide and ammonium carbamate respectively; and he was also interested in the method of determining the vapor pressure of sodium sulphate decahydrate with the aid of isoamyl alcohol.

The author has produced a first-class laboratory manual of the orthodox type. The absence of informal but interesting qualitative experiments is a disappointment to the reviewer, believing as he does that a modicum of experiments of this kind serves to stimulate in the student a spirit of inquiry, without producing any very disastrous consequences. This criticism, however, represents only a point of view and reflects in no wise on a very useful and creditable work. *T. R. Briggs*

THE AMMONIUM CARBAMATE EQUILIBRIUM

BY T. R. BRIGGS AND V. MIGRDICHIAN

The equilibrium between ammonia, carbon dioxide and ammonium carbamate has been made the subject of several investigations,[1] some of which, particularly those by Horstmann and by Isambert, are regarded as classic. A critical study of the data, however, reveals the fact that the latter are far from satisfactory and confirm the Mass Law only roughly. That this should be the case is not so surprising when one considers that the data were obtained more than forty years ago; but it is surprising to find that nobody heretofore has taken the trouble to repeat the work with care and reasonable accuracy. Professor Bancroft brought this point to our attention, and the present investigation was undertaken.

The experimental procedure employed may be said briefly to consist in measuring, at constant volume and at definite temperatures (10°, 15°, 20°, 25°, 30°, 35°, 40°, 45°) the pressure exerted by the vapor phase in equilibrium with solid ammonium carbamate, when the latter is brought into contact with a definite quantity of ammonia or of carbon dioxide.

Theoretical

Solid ammonium carbamate is volatile at ordinary temperatures and Naumann,[2] from determinations of the vapor density, has shown conclusively that the vapor consists wholly of ammonia and carbon dioxide, at least above 37°. At higher temperatures (130°) the solid carbamate loses water and changes to urea[3]; but at the temperatures employed in this work (10° to 45°) the formation of urea may safely be regarded as inappreciable.

When solid carbamate is vaporized and brought into equilibrium with the dissociated vapor, the state of the system may be represented as follows:

$$\underline{NH_4NH_2CO_2} \rightleftarrows 2\overline{NH_3} + \overline{CO_2} \tag{1}$$

For such a case, the Mass Law requires the following relation between the partial pressures of ammonia and carbon dioxide:

$$p^2NH_3 . pCO_2 = K_p \tag{2}$$

and since dissociation occurs with an absorption of heat, K_p will increase as the temperature is raised.

If one starts with pure carbamate and causes it partially to vaporize, the system solid and vapor is univariant and at any one temperature there can

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[1] Bineau: Ann. chim. phys. (2) 67, 240 (1838); Rose: Pogg. Ann. 46, 363 (1839); Naumann: Ann. 160, 1 (1871); Horstmann: Ibid. 187, 148 (1877); Isambert: Compt. rend. 92, 919; 93, 731 (1881); 96, 340 (1882); 97, 1212 (1883); Briner: J. Chim. phys. 4, 276 (1906).

[2] Ann. 160, 1 (1871).

[3] Basarow: Bull. (4) 32, 394 (1922).

be but one equilibrium pressure. This pressure is the normal dissociation pressure and it will be represented by π_o. If the carbamate vapor is completely dissociated into ammonia and carbon dioxide, then

$$pNH_3 = \frac{2\pi_o}{3}, \text{ and } pCO_2 = \frac{\pi_o}{3}$$

On substituting these values in (2), the following expression is obtained:

$$\frac{4}{27}\pi^3_o = K_p \qquad (3)$$

When, however, carbamate is vaporized into a space containing either ammonia or carbon dioxide, (or both, in any volume-ratio other than 2 NH_3: 1 CO_2) the system solid and vapor is bivariant and there can be different equilibrium pressures at any one temperature depending upon the composition of the vapor phase. Suppose one introduces solid carbamate into a space containing ammonia, the pressure of which is e_1. Let the total vapor pressure at equilibrium be represented by P. Then $P-e_1$ is the partial pressure of the 'carbamate' vapor, and since the latter is presumed to be completely dissociated

$$pNH_3 = \frac{2(P-e_1)}{3} + e_1 = \frac{2P+e_1}{3} \qquad (4)$$

$$\text{and } pCO_2 = \frac{P-e_1}{3} \qquad (5)$$

providing, of course, the space occupied by the solid carbamate itself is small enough to be disregarded. On substituting these expressions for pNH_3 and pCO_2 in (2), one arrives at the following working relation:

$$\left(\frac{2P+e_1}{3}\right)^2 \cdot \frac{P-e_1}{3} = K_p \qquad (6)$$

When carbon dioxide at a pressure e_2 is used in place of ammonia, the relation becomes:

$$\left(\frac{2P-2e_2}{3}\right)^2 \cdot \frac{P+2e_2}{3} = K_p \qquad (7)$$

By employing Equations (3), (6) and (7), the equilibrium constant has been determined in this investigation under three different sets of experimental conditions—(1) when the vapor consisted wholly of dissociated ammonium carbamate, (2) when the vapor contained ammonia in excess, (3) when the vapor contained carbon dioxide in excess. The first method necessitated careful redetermination of the normal dissociation pressure π_o of pure ammonium carbamate, while the other two methods required the measurement of the total equilibrium pressure when the excess of ammonia or carbon dioxide was known.

A further interesting relation may be brought out as follows. If the partial pressure of dissociated carbamate in the vapor be represented by π, then since $\pi = P-e_1 = P-e_2$,

$$\left(\frac{2\pi}{3}+e_1\right)^2\frac{\pi}{3}=\frac{4}{27}\pi_0^3,$$

and

$$\left(\frac{2\pi}{3}\right)^2\left(\frac{\pi}{3}+e_2\right)=\frac{4}{27}\pi_0^3$$

Dividing both members of each equation by π_0^3, we obtain the following:

$$\left(\frac{2\pi}{3\pi_0}+\frac{e_1}{\pi_0}\right)^2\frac{\pi}{3\pi_0}=\frac{4}{27},$$

and

$$\left(\frac{2\pi}{3\pi_0}\right)^2\left(\frac{\pi}{3\pi_0}+\frac{e_2}{\pi_0}\right)=\frac{4}{27}$$

whence

$$\frac{e_1}{\pi_0}=\frac{2}{3}\left[\left(\frac{\pi_0}{\pi}\right)^{\frac{1}{2}}-\frac{\pi}{\pi_0}\right] \qquad (8)$$

and

$$\frac{e_2}{\pi_0}=\frac{1}{3}\left[\left(\frac{\pi_0}{\pi}\right)^2-\frac{\pi}{\pi_0}\right] \qquad (9)$$

These equations in e/π_0 and π/π_0 are independent of the equilibrium constant K_p and therefore of the temperature at which equilibrium prevails. By assigning definite values between 0 and 1 to π/π_0, corresponding values of e/π_0 have been computed, and curves—one for ammonia and one for carbon dioxide—have been drawn with the data thus obtained. Each of these curves (Figs. 2 and 3) is therefore the graph of the Mass Law applied to the particular case and each suffices in theory for all temperatures. Similar curves have been displayed by Horstmann, but it is a particular purpose of this investigation to ascertain how closely the experimentally determined values of π/π_0 and e/π_0 agree with those calculated from the Mass Law Equations (8) and (9).

Experimental

Preparation of the Pure Materials

The ammonia was obtained from cylinders of the compressed gas. It was dried with great care by passing it over calcium oxide, then over solid sodium hydroxide and finally over metallic sodium. The gas thus treated was found to contain less than one-tenth of one percent of residue unabsorbable by sulphuric acid.

The carbon dioxide was prepared from pure marble in a specially designed generating apparatus, and was dried by being passed through two Friedrichs bottles containing sulphuric acid, followed by two U tubes filled with phosphorus pentoxide. The gas was found to be free from hydrochloric acid vapor and was absorbed completely by a solution of sodium hydroxide.

Pure ammonium carbamate was prepared by allowing dry ammonia and dry carbon dioxide, in the proper volume-ratio, to react in a special chamber cooled to 0°. The carbamate was preserved in this chamber out of contact with moisture and air.

Apparatus and Procedure

The general disposition of the dissociation apparatus is shown in Figure 1. *B* is the reaction chamber and M_1M_2 the manometer. The volume of *B* was maintained constant by means of the adjustable mercury seal *U* in the lower arm of the bulb. Sealed into *B* at its upper end was a capillary tube containing a glass stop cock, through which ammonia or carbon dioxide could be introduced, as desired. Solid ammonium carbamate was stored in the side-arm *A* and was kept completely covered with mercury, by means of a procedure to be described later.

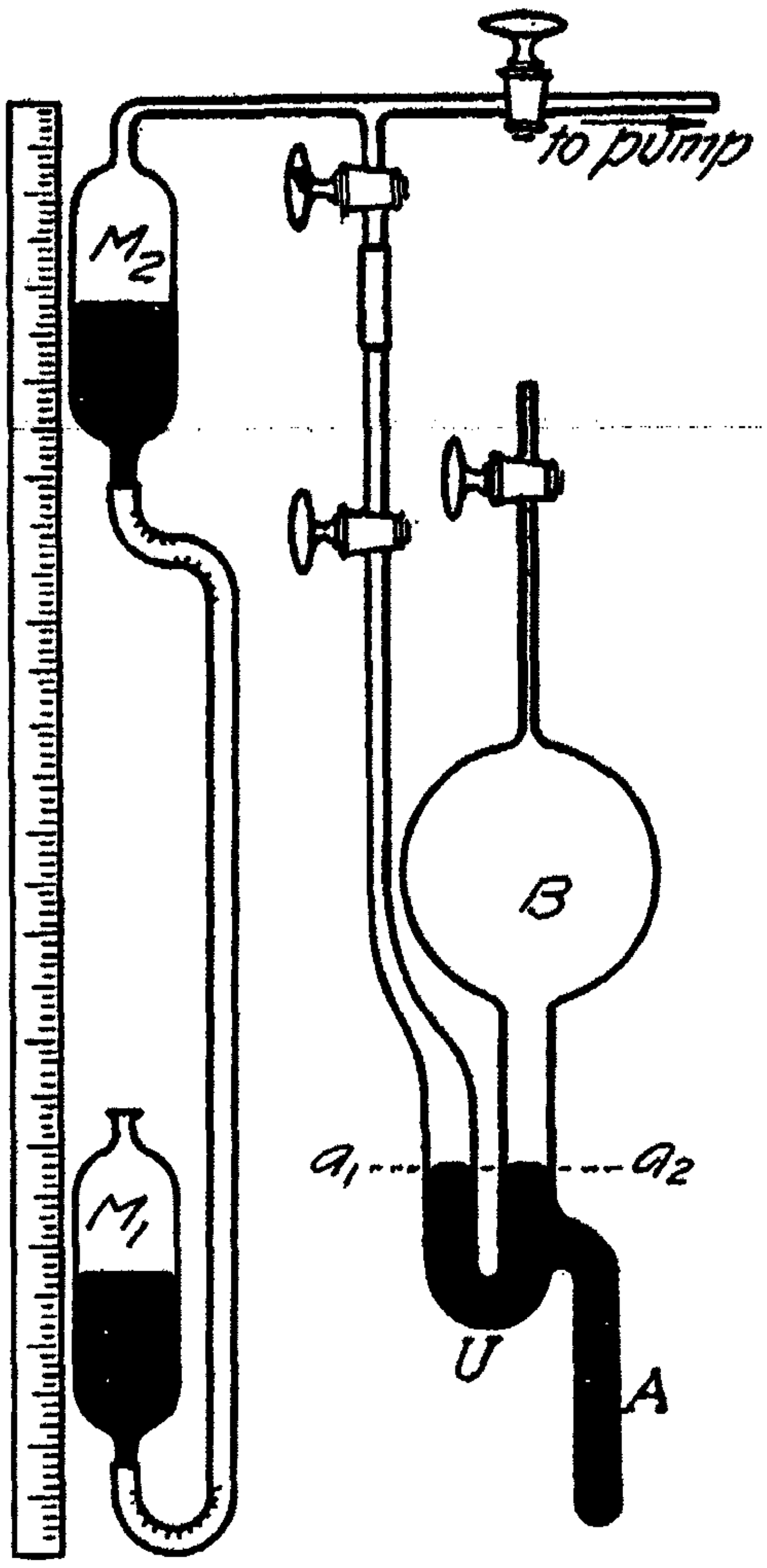

Fig. 1

The pressure in *B* (always less than one atmosphere) was measured by means of the manometer M_1M_2 and a carefully calibrated barometer. When the mercury in each arm of *U* was brought to the same level, the pressure above the mercury in M_2 was exactly equal to the pressure in B and this in turn was found by subtracting from the barometric pressure the pressure of the column of mercury between M_1 and M_2. The accurate adjustment of levels in U was performed by raising or lowering M_2 by means of a special screw until the surfaces a_1 and a_2 were at exactly the same level, as ascertained by sighting along a horizontal line in a telescope. The length of the column of mercury between M_1 and M_2 was measured against a fixed scale by determining the position of the mercury in M_1 and M_2, with the aid of a cathetometer. The usual corrections for temperature were applied to all manometric and barometric readings.

The reaction bulb B was immersed up to the stopcock in a water thermostat, electrically heated, stirred and regulated. The temperature seldom varied by more than 0.05° over a period of eight hours, six hours being found ample above 15° for the establishment of equilibrium.

A thermometer, calibrated by the Bureau of Standards, and permitting readings of temperature to 0.01°, was immersed in the bath near the bulb B. Readings at stated intervals were taken and these were averaged in obtaining the equilibrium temperature.

In order to carry out the necessary measurements with one of the gases—ammonia or carbon dioxide—present in excess in the reaction chamber B, it was first necessary to obtain a sufficient supply of the dry solid carbamate in the side arm A, before the excess of gas was introduced into B. Carbamate was first sublimed into B by connecting the latter to the cylinder in which was stored the dry reagent prepared as previously stated. A small cooling jacket was then fitted about the side arm A and the whole apparatus was immersed in hot water. Carbamate soon gathered in the side arm and in a few hours appeared to have been eliminated completely from B and from U, and to have been localized wholly in A. Thereupon the carbamate in A was covered with a column of mercury and the last traces of carbamate in the rest of the apparatus were removed by repeated evacuation.

The whole apparatus was then filled with mercury which had previously been freed from air and moisture by being heated to 200° under reduced pressure. A suitable quantity of ammonia or carbon dioxide was next introduced and enough mercury was left in the apparatus to serve as the seal and pressure indicator in U. The whole was then placed in the thermostat at 20° and the pressure of the gas determined. Care was taken to see that the carbamate in the side arm was covered with mercury to a sufficient depth so as to prevent sublimation into B. Since the pressure of the gas in B remained constant with time, no sublimation could have occurred, for had it done so, a marked increase in pressure would have been observed.

The bulb B was next removed from the thermostat and the side arm A was heated carefully so as to distill carbamate back into the reaction chamber, after the latter had been filled with ammonia or carbon dioxide at known pressure. A small quantity of the reagent passed into B, where it condensed on the walls. Care was taken to heat locally the walls of the *U* tube containing the mercury seal, so as to free them from condensed carbamate. The apparatus was then returned to the thermostat and allowed to remain for several hours until the pressure became constant and equilibrium was presumably established. The total pressure in *B* was finally ascertained as carefully as possible. Different determinations of pressure varied by not more than 0.3 mm. Equilibrium pressures were determined at 10°, 15°, 20°, 25°, 30°, 35°, 40°, and 45°. In all, twelve such complete runs were carried out, six with ammonia in excess, five with carbon dioxide and one with no excess of either component. The complete investigation thus included some ninety independent determinations of the equilibrium pressure, although in a few cases several of the above temperatures were passed by.

The pressure of the gas in excess, in the absence of carbamate, was determined at 20° for each of the twelve runs. From this value the pressure of the gas in excess was computed for the other temperatures by assuming that the pressure, at constant volume, varied directly with the absolute temperature. Special experiments showed that this was true, as the pressures were never very great. No correction was made for the expansion of the bulb, as these special experiments indicated that this was an unnecesary refinement under the conditions of the work.

Special care was taken, however, to eliminate the errors that might be caused by air adsorbed in the carbamate or by the walls of the reaction chamber. The carbamate was stored *in vacuo* and no air was allowed at any time to enter the reaction chamber, after the air had once been removed completely by heating under reduced pressure.

Special experiments were also carried out for the purpose of redetermining the dissociation pressures of ammonium carbamate between 10° and 45°. These measurements were carried out in the equilibrium apparatus just described. Carbamate was sublimed into the reaction chamber *B*, and the latter was then filled with dry, air-free mercury. On closing the upper stopcock and withdrawing mercury, the carbamate was caused to vaporize in *B*, this process being hastened by heating. The vapor so formed was next condensed to the solid by compression, the bulb *B* was again filled with mercury and the slight trace of uncondensable gas was trapped in the upper capillary and expelled through the stopcock. The mercury was again run out and the carbamate was once more vaporized in the reaction chamber. The condensation to solid was repeated, and the cycle of evaporation and condensation was continued until no trace of uncondensable residue could be detected. The bulb *B* containing pure carbamate was then placed in the thermostat and the equilibrium pressure was determined. Needless to say, the glass stopcock was tested and was found to be free from leaks.

The Dissociation Pressure of Ammonium Carbamate

The data, obtained as described, have been assembled in Table I. Pressure is stated in millimeters, temperature in degrees Centigrade.

TABLE I

The Dissociation Pressure of Ammonium Carbamate

Temp.	π_0	Temp.	π_0	Temp.	π_0	Temp.	π_0
10.03	29.2	24.91	88.3	29.83	124.5	36.90	199.1
10.92	31.4	25.33	92.0	29.96	124.5	37.88	212.9
14.92	42.5	25.88	94.2	30.91	133.6	38.87	226.7
16.90	49.3	26.77	100.3	32.10	145.0	39.89	242.5
17.86	52.7	26.92	101.3	32.91	153.4	41.91	276.3
19.87	61.3	27.85	108.3	33.90	163.3	44.86	331.6
21.25	68.1	28.87	114.1	34.89	174.9		
22.96	77.0	28.92	116.7	35.91	186.7		

The values of π_0 and t were next plotted and a pressure-temperature curve, several feet in length, was constructed, each centimeter on the temperature axis representing 0.2°, and each centimeter on the π_0 axis a pressure of 5 mm. The individual determinations lay very close to a smooth curve, while the dissociation pressures reported by Horstmann, Naumann and Isambert, plotted for comparison, showed irregular variations and were in general greater than ours. By constructing the curve on so generous a scale it became possible to read from the curve values of π_0 with great precision (to 0.2 mm.).

The Dissociation Pressure With One Component in Excess

In accordance with the procedure described, twelve different series of determinations were carried out, six of these with ammonia in excess, five with carbon dioxide, and one with pure carbamate as a check. The pressure of the gas in excess was measured at 20° in each series and the pressure at other temperatures was computed from this value. Each series was run in general at 5° intervals from 10° to 45° inclusive. The data have been assembled in Table II, the symbols having in every case the meaning already assigned to them. The series are numbered in the first column.

The equilibrium constant K_p has been computed in two ways—in Column 8 from the product $p^2NH_3 . p\ CO_2$ and in Column 9 from $4/27\ \pi_0^3$, the values of π_0 having been read from the dissociation pressure curve. The agreement is satisfactory, except for the runs at 10°, though in general the values of K_p computed from the product of the partial pressures are slightly smaller than those obtained from the dissociation curve. We do not feel justified in regarding this difference as significant at the present time, since in general the variations in K_p that may be observed in the table do not greatly exceed the probable error involved in these measurements.

TABLE II
Equilibrium Data and Dissociation Constants

(1) Exp. No.	(2) Temp. °C	(3) e_1	(4) e_2	(5) P	(6) pNH_3	(7) pCO_2	(8) $K_p/10^3$	(9) $\frac{4}{27}\pi_0^3/10^3$
A1	10.04	157.5		158.3	158.0	0.26	6.5	3.7
A2	10.08	131.8		132.2	132.1	0.13	2.2	3.8
A3	10.01	52.4		57.2	55.6	1.6	5.0	3.7
A4	10.05	49.0		56.4	53.9	2.5	7.3	3.7
A5	10.41	25.5		36.3	32.7	3.6	3.9	4.1
A6	10.04	12.7		34.3	27.1	7.2	5.3	3.7
A7	10.03	0	0	29.2	19.4	9.7	3.7	3.7
A8	10.00		19.3	39.6	13.5	26.1	4.8	3.7
A9	10.18		33.4	48.7	10.2	38.5	4.0	3.9
A10	10.01		87.1	97.1	6.7	90.4	4.1	3.7
A11	10.00		158.0	165.1	4.7	160.4	3.5	3.7
A12	10.06		159.1	166.9	5.2	161.7	4.4	3.8
B1	14.89	160.2		162.1	165.1	0.63	16.4	11.3
B2	14.93	134.1		137.1	136.1	1.0	18.5	11.3
B3	14.92	53.3		63.3	60.0	3.3	11.9	11.3
B4								
B5	14.93	25.9		46.7	39.8	6.9	10.9	11.3
B6	14.88	12.9		42.1	32.4	9.7	10.2	11.3
B7	15.00	0	0	43.1	28.7	14.4	11.8	11.5
B8	14.85		19.7	48.6	19.3	29.3	10.9	11.2
B9	14.92		34.0	58.0	16.0	42.0	10.8	11.3
B10	15.00		88.6	105.7	11.4	94.3	12.3	11.5
B11	15.00		160.9	173.1	8.1	165.0	10.8	11.5
B12	14.91		161.9	174.5	8.4	166.1	11.7	11.3
C1	19.93	163.0		166.6	165.4	1.2	32.8	34.7
C2	19.93	136.4		141.7	139.9	1.8	35.2	34.7
C3	19.92	54.2		75.9	68.7	7.2	34.0	34.6
C4	19.89	50.7		73.0	65.6	7.4	31.8	34.4
C5	19.94	26.4		64.2	51.6	12.6	33.6	34.8
C6	19.89	13.1		63.1	46.4	16.7	36.0	34.4
C7	20.00	0	0	61.8	41.2	20.6	35.0	35.3
C8	19.95		20.0	66.1	30.7	35.4	33.4	34.9
C9	19.91		34.6	74.4	26.5	47.9	33.6	34.6
C10	19.86		90.1	118.3	18.8	99.5	35.2	34.1
C11	19.91		163.6	184.9	14.2	170.7	34.4	34.6
C12	19.86		164.7	185.3	13.7	171.6	32.3	34.1
D1	24.98	165.7		176.4	172.8	3.6	107.2	102.7
D2	24.91	138.7		152.4	147.8	4.6	100.5	100.7
D3	24.89	55.2		98.1	83.8	14.3	100.4	101.1
D4								
D5	24.94	26.9		89.4	68.6	20.8	97.9	101.5
D6	24.94	13.3		88.1	63.2	24.9	99.5	101.5
D7	25.00	0	0	88.5	59.0	29.5	102.7	103.3
D8	24.88		20.4	90.2	46.5	43.7	94.9	99.8
D9	24.88		35.2	97.4	41.5	55.9	69.3	99.8
D10	24.86		91.7	137.3	30.4	106.9	98.8	99.2
D11	24.94		166.5	201.1	23.1	178.0	95.0	101.5
D12	24.89		167.5	202.4	23.3	179.1	97.2	99.9

Table II (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
E1	30.01	168.6		194.2	185.7	8.5	293	294
E2	29.96	141.1		174.2	163.2	11.0	293	291
E3	29.95	56.1		132.2	106.8	25.4	289	289
E4	29.94	52.5		129.5	103.8	25.7	277	289
E5	29.93	27.3		125.4	92.7	32.7	281	288
E6	29.96	13.6		124.9	87.8	37.1	286	290
E7	30.00	0	0	125.0	83.3	41.7	289	293
E8	29.93		20.7	126.8	70.7	56.1	280	288
E9	29.92		35.8	132.4	64.4	68.0	282	287
E10	29.90		93.3	165.9	48.4	117.5	275	285
E11	29.85		169.2	226.6	38.3	188.3	276	283
E12	29.93		170.4	227.3	37.9	189.4	272	288
F1	34.92	171.3		226.2	207.9	18.3	791	798
F2	34.88	143.5		210.9	188.4	22.5	799	790
F3	34.91	56.9		180.0	139.0	41.0	792	796
F4								
F5	34.86	27.7		174.2	125.4	48.8	767	789
F6	34.94	13.8		174.5	120.9	53.6	783	800
F7	35.00	0	0	175.9	117.3	58.6	806	810
F8	34.90		21.1	175.7	103.7	72.6	771	794
F9	34.76		36.4	178.8	94.9	83.9	756	773
F10	34.85		94.8	208.2	78.9	129.3	758	787
F11	34.81		172.0	263.7	61.1	202.6	757	780
F12	34.90		173.2	265.2	61.3	203.9	767	794
G1	39.89	174.1		279.8	244.6	35.2	2106	2116
G2	39.90	145.7		270.9	229.2	41.7	2190	2120
G3	39.94	57.9		246.4	183.6	62.8	2117	2136
G4	39.87	54.1		244.3	181.3	63.0	2071	2108
G5	39.84	28.3		241.5	170.4	71.1	2065	2096
G6	39.85	14.0		240.9	165.3	75.6	2066	2100
G7	40.00	0	0	244.3	162.9	81.4	2160	2160
G8	39.90		21.4	243.5	148.0	95.5	2091	2120
G9	39.87		37.0	246.6	139.7	106.9	2086	2108
G10	39.80		96.4	268.7	114.9	153.8	2030	2080
G11	39.85		174.9	319.5	96.4	223.1	2073	2100
G12	39.87		176.1	320.1	96.0	224.1	2065	2108
H1	44.93	176.8		358.8	298.1	60.7	5394	5476
H2	44.84	148.1		352.5	284.4	68.1	5508	5384
H3								
H4	44.84	55.0		332.9	240.3	92.6	5347	5384
H5	44.84	28.7		332.2	231.3	101.7	5441	5384
H6	44.89	14.3		331.7	225.9	105.8	5399	5436
H7	45.00	0	0	334.4	222.9	111.5	5540	5545
H8	44.88		21.8	332.0	206.8	125.2	5354	5426
H9	44.82		38.7	333.0	196.5	137.0	5290	5363
H10	44.85		98.0	351.0	168.7	182.3	5188	5395
H11	44.97		177.8	397.9	146.7	251.2	5407	5515
H12	44.83		178.9	396.8	145.3	251.5	5310	5374

Values of e/π_0 and π/π_0 computed from the experimental data of Table II have been assembled in Table III. For convenience the number of each experiment has been repeated in the first column of data, and likewise the values of e_1 and e_2 in Columns 2 and 3.

TABLE III

Comparison between $\frac{\pi}{\pi_0}$ Found, and $\frac{\pi}{\pi_0}$ Required by Mass Law

(1) Exp. No.	(2) e_1	(3) e_2	(4) π	(5) π_0	(6) $\frac{e}{\pi_0}$	(7) $\frac{\pi}{\pi_0}$ Found	(8) $\frac{\pi}{\pi_0}$ Mass Law
A1	157.5		0.8	29.1	5.42	0.03	0.01
A2	131.8		0.4	29.2	4.52	0.01	0.02
A3	52.4		4.8	29.0	1.81	0.17	0.13
A4	49.0		7.4	29.1	1.68	0.25	0.14
A5	25.5		10.8	30.0	0.85	0.36	0.37
A6	12.7		21.6	29.1	0.44	0.74	0.62
A7	0	0	29.2	29.0	0	1	1
A8		19.3	20.3	29.0	0.67	0.70	0.62
A9		33.4	15.3	29.5	1.13	0.52	0.51
A10		87.1	10.1	29.0	3.00	0.35	0.33
A11		158.0	7.1	29.0	5.44	0.25	0.25
A12		159.1	7.8	29.2	5.44	0.27	0.25
B1	160.2		1.9	42.4	3.78	0.05	0.03
B2	134.1		3.0	42.5	3.15	0.07	0.05
B3	53.3		10.0	42.5	1.25	0.24	0.23
B4							
B5	25.9		20.8	42.5	0.61	0.49	0.50
B6	12.9		29.2	42.4	0.30	0.69	0.73
B7	0	0	43.1	42.8	0	1	1
B8		19.7	28.9	42.3	0.47	0.68	0.69
B9		34.0	24.0	42.5	0.80	0.57	0.58
B10		88.6	17.1	42.8	2.07	0.40	0.39
B11		160.9	12.2	42.8	3.75	0.29	0.30
B12		161.9	12.6	42.5	3.78	0.30	0.30
C1	163.0		3.6	61.7	2.64	0.06	0.06
C2	136.4		5.3	61.7	2.21	0.09	0.09
C3	54.2		21.7	61.7	0.88	0.35	0.36
C4	50.7		22.3	61.5	0.83	0.36	0.39
C5	26.4		37.8	61.8	0.43	0.61	0.62
C6	13.1		50.0	61.5	0.21	0.82	0.80
C7	0	0	61.8	62.0	0	1	1
C8		20.0	46.1	61.8	0.32	0.75	0.76
C9		34.6	39.8	61.6	0.56	0.65	0.65
C10		90.1	28.2	61.5	1.47	0.46	0.45
C11		163.6	21.3	61.6	2.64	0.35	0.35
C12		164.7	20.6	61.5	2.67	0.34	0.34

Table III (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
D1	165.7		10.7	89.0	1.86	0.12	0.11
D2	138.7		13.7	88.5	1.57	0.16	0.16
D3	55.2		42.9	88.5	0.62	0.48	0.49
D4							
D5	26.9		62.5	88.7	0.30	0.71	0.73
D6	13.3		74.8	88.7	0.15	0.84	0.86
D7	0	0	88.5	89.0	0	1	1
D8		20.4	69.8	88.4	0.24	0.79	0.82
D9		35.2	62.2	88.4	0.40	0.70	0.72
D10		91.7	45.6	88.3	1.04	0.52	0.53
D11		166.5	34.6	88.7	1.88	0.39	0.40
D12		167.5	34.9	88.5	1.90	0.39	0.40
E1	168.6		25.6	125.5	1.34	0.20	0.21
E2	141.1		33.1	125.0	1.13	0.26	0.27
E3	56.1		76.1	125.0	0.45	0.61	0.61
E4	52.5		77.0	125.0	0.42	0.62	0.63
E5	27.3		98.1	124.7	0.22	0.79	0.80
E6	13.6		111.3	125.0	0.11	0.89	0.89
E7	0	0	125.0	125.5	0	1	1
E8		20.7	106.1	124.7	0.17	0.85	0.86
E9		35.8	96.6	124.7	0.29	0.77	0.78
E10		93.3	72.6	124.5	0.75	0.58	0.59
E11		169.2	57.4	124.2	1.36	0.47	0.47
E12		170.4	56.9	124.7	1.37	0.46	0.47
F1	171.3		54.9	175.2	0.92	0.31	0.32
F2	143.5		67.4	174.8	0.82	0.39	0.39
F3	56.9		123.1	175.0	0.33	0.70	0.71
F4							
F5	27.7		146.5	174.5	0.16	0.84	0.85
F6	13.8		160.7	175.5	0.08	0.92	0.92
F7	0	0	175.9	176.2	0	1	1
F8		21.1	154.6	175.0	0.12	0.89	0.90
F9		36.4	142.4	173.5	0.21	0.82	0.83
F10		94.8	113.4	174.5	0.54	0.65	0.66
F11		172.0	91.7	174.0	0.99	0.53	0.53
F12		173.2	92.0	175.0	0.99	0.53	0.53
G1	174.1		105.7	242.5	0.72	0.44	0.44
G2	145.7		125.2	243.0	0.60	0.51	0.51
G3	57.9		188.5	243.5	0.24	0.77	0.78
G4	54.1		189.2	242.3	0.22	0.78	0.80
G5	28.3		213.2	242.0	0.12	0.88	0.89
G6	14.0		226.9	242.0	0.06	0.94	0.94
G7	0	0	244.3	244.4	0	1	1
G8		21.4	221.1	243.0	0.09	0.91	0.92
G9		37.0	209.6	242.3	0.15	0.87	0.87
G10		96.4	172.3	241.2	0.40	0.72	0.72
G11		174.9	144.6	242.0	0.72	0.60	0.60
G12		176.1	144.0	242.3	0.73	0.59	0.60

Table III (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
H1	176.8		182.0	333	0.53	0.54	0.55
H2	148.1		204.4	331	0.45	0.62	0.61
H3							
H4	55.0		277.9	331	0.17	0.84	0.85
H5	28.7		303.5	331	0.09	0.92	0.92
H6	14.3		317.4	332	0.04	0.96	0.96
H7	0	0	334.4	334.5	0	1	1
H8		21.8	310.2	332	0.07	0.94	0.94
H9		38.7	294.8	331	0.12	0.89	0.90
H10		98.0	253.0	331.5	0.30	0.76	0.78
H11		177.8	220.1	334	0.53	0.66	0.67
H12		178.9	217.7	331	0.54	0.66	0.66

In Figure 2 (and also in Figure 3) the graphs of Equations (8) and (9) have been displayed in accordance with the statement made during the discussion of the theory. From these curves, therefore, may be read values of π/π_0 corresponding in theory to the various *experimental* values of e/π_0. The theoretical values of π/π_0 thus read from the curves have been assembled

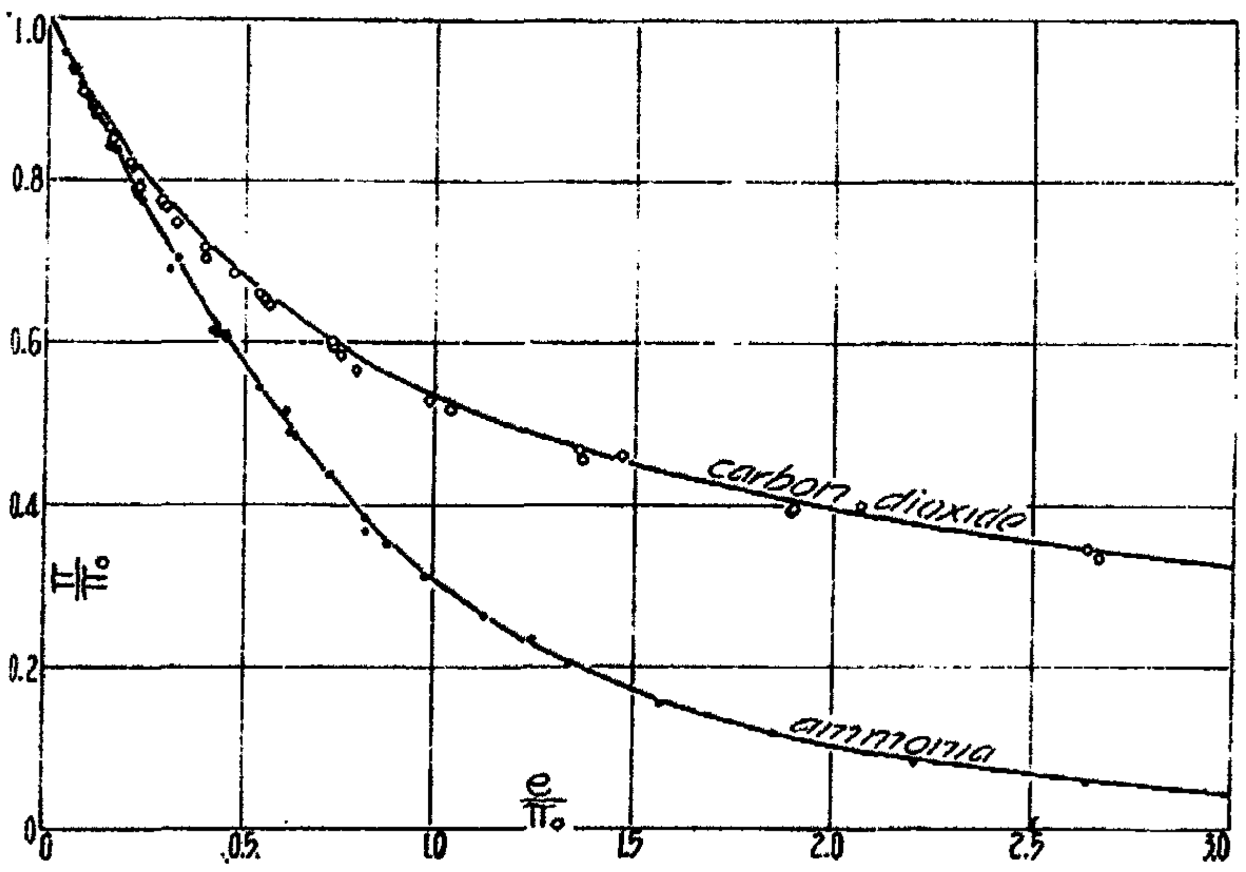

Fig. 2

in the last column of data in Table III, where they may be compared with the values of π/π_0 obtained by experiment. The close agreement between the two sets of values shows how nearly the experimental data are in accord with the Mass Law.

To bring out this point more strikingly, the values of π/π_0 and $\frac{e}{\pi_0}$ obtained *by experiment* have been plotted in Figure 2, ammonia in excess being distinguished from carbon dioxide in excess by the full black circles. It will be seen that the points lie on, or very close to, the corresponding Mass Law curves.

The results at 10° are less satisfactory and have not been plotted in Figure 2, since equilibrium was possibly not attained in this series of determinations. It should also be stated that the values of e/π_0 and π/π_0 in Table III have been rounded off as regards the third decimal.

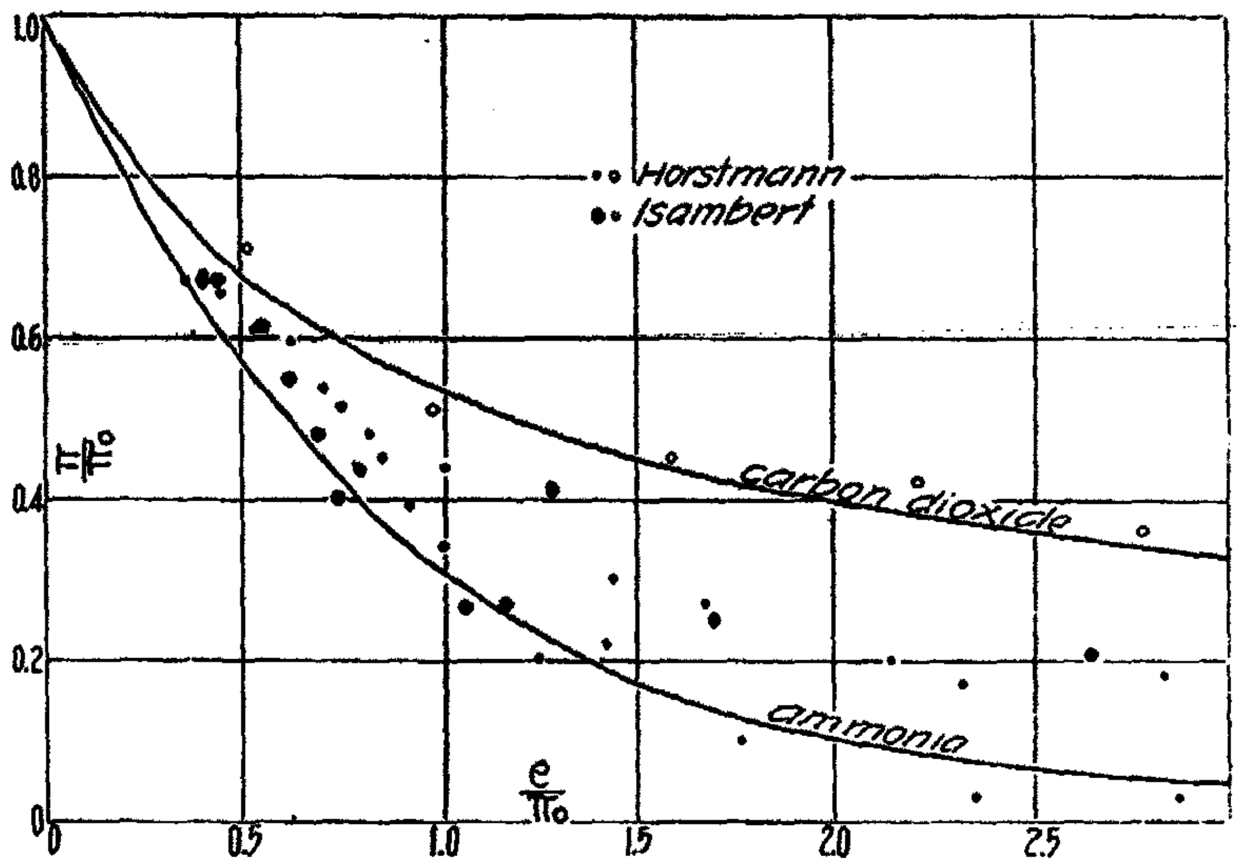

FIG. 3

An interesting point is brought out by the curves shown in Figure 2. For small values of e/π_0, particularly when e represents the excess of ammonia,

$$e/\pi_0 = 1 - \pi/\pi_0 \text{ (approximately)},$$

whence

$$e = \pi_0 - \pi \text{ (approximately)},$$

and since

$$P = \pi + e,$$
$$P = \pi_0 \text{ (approximately)}.$$

That is, the total equilibrium pressure obtained when the solid carbamate is in contact with vapor containing a small 'relative' excess of ammonia or carbon dioxide (e/π_0 less than 0.1) is approximately equal to the normal dissociation pressure of the pure carbamate. It follows from this that at high temperatures one may add a fairly large amount of ammonia or carbon dioxide to carbamate in contact with its vapor without causing any marked increase in the total pressure of the vapor. A glance at the values of P (Table II, Column 5) show that such is the case at the higher temperatures when e is small. As a matter of fact however, the Mass Law requires that P be a minimum when e is zero, as Briner[1] has pointed out.

For the purpose of comparison, values of e/π_0 and π/π_0 computed from Horstmann's data have been plotted in Figure 3 on the same scale as that employed in Figure 2, the full black circles representing ammonia in excess, as before. It is evident that these values, all of which were obtained in the neighborhood of 20°, are not satisfactory, particularly when ammonia is present in excess, though the values with carbon dioxide are in better agreement with the theory.

Isambert's results have also been displayed in Figure 3, the values of e/π_0 and π/π_0 having been calculated from the original data.[2] A glance will suffice to show that these data, likewise, can hardly be looked upon as confirming the Mass Law.

Isambert[3] at a later date reported results that were much more accurately obtained. Unfortunately the experimental data were not reported, but only values of π_0 computed from the relation:

$$\pi_0 = \sqrt[3]{\frac{27}{4} p^2 NH_3 . pCO_2} \qquad (10).$$

TABLE IV

Temp.	Isambert's Data: Values of $\sqrt[3]{\frac{27}{4} p^2 NH_3 \, pCO_2}$				π_0 from Dissociation Curve
	129 CO_2	61 CO_2	60 NH_3	114 NH_3 in excess	
34.0	170	165	167	181	165
37.2	211	205	206	216	204
41.8	272	268	266	275	274
46.9	375	372	376	378	
52.6	524	522	524	526	

Temp.	Present Data: Values of $\sqrt[3]{\frac{27}{4} p^2 NH_3 \, p\,CO_2}$				π_0 from Dissociation Curve
	160-180 CO_2	34-39 CO_2	55-59 NH_3	140-178 NH_3 in excess	
20.0	61.9	61.4	61.6	60.9	62.0
25.0	88.2	87.7	88.5	88.0	89.0
30.0	124.5	124.8	125.5	125.0	125.5
35.0	174.5	174.9	175.9	176.8	176.2
40.0	242.7	243.5	243.7	243.7	244.4
45.0	333.2	333.0	333.8	332.9	334.5

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[1] J. Chim. phys. 4, 276 (1906).

[2] Compt. rend. 93, 731 (1881); Ostwald: "Lehrbuch", II (2) 523.

[3] Compt. rend. 97, 1212 (1883).

In Table IV are recorded Isambert's values of π_0 calculated from Equation (10), and for comparison some values computed in a like manner from the data obtained in the present investigation, by employing the same equation. It should be noted that the values of $K_p = p^2NH_3 \cdot pCO_2$ (taken from Column 8 of Table II) have been reduced to the proper temperature by adding a correction ascertained from the temperature variation in the values of $^4/_{27}\pi_0^3$ recorded in Column 9 of Table II. The values of π_0 have been computed from determinations in which either carbon dioxide or ammonia was in excess as stated. All values are expressed in mm.

These later determinations by Isambert agree much more closely with the Mass Law, and in some cases remarkably so. Nevertheless Isambert's calculated values of π_0 differ among themselves rather widely, much more so than do the values of π_0 computed from the equilibrium pressures in this investigation, though the latter values in general are slightly smaller than the normal dissociation pressures obtained directly with carbamate alone.

Briner's data have not been considered because they were obtained at rather high temperatures and are not very numerous. They can be regarded, however, as approximately confirming the Mass Law.

Summary

(1). Previous investigations of the ammonium carbamate equilibrium from the point of view of the Mass Law have for the most part yielded incomplete or unsatisfactory results.

(2). The ammonium carbamate equilibrium has been studied at low pressures and at several temperatures between 10° and 45°.

(3). The dissociation pressures of pure ammonium carbamate have been redetermined with great care between 10° and 45°.

(4). Except at the lowest temperature employed, the ammonium carbamate equilibrium has been found to conform to the Mass Law, within the limits of experimental accuracy.

Cornell University
March, 1924

THE CATALYTIC ACTIVITY OF CARBONS FROM AROMATIC HYDROCARBONS AND SOME DERIVATIVES

BY WALTER FARMER AND JAMES BRIERLEY FIRTH

A study of the catalytic activity of cane sugar carbon relative do hydrogen peroxide[1] showed that the activity is influenced by the previous treatment of the carbon. Subsequently, it was shown[2] that the influence of the previous treatment of the carbon upon the catalytic activity with reference to hydrogen peroxide manifested itself in the case of carbons prepared from ten carbohydrates other than cane sugar. The same authors[3] not only adduced evidence to show that the rate and extent of the catalytic decomposition of aqueous hydrogen peroxide by pure sugar carbon is increased with rise of temperature, but also showed that the activity of the carbon decays during the reaction. This phenomenon was made clear when it was shown that the fundamental difference in the activity of the carbons derived from carbohydrates manifested itself in the initial activity. This activity rapidly fell off after the first few minutes, ultimately becoming very slight, notwithstanding that the solution contained a considerable quantity of undecomposed hydrogen peroxide. In the same paper (loc.cit.) experiments were described in which cellulose carbon, after iodine treatment, exhibited a remarkable increase in the initial activity towards aqueous hydrogen peroxide, the concentration of the solution and the conditions of temperature remaining constant for all experiments. Thus, after heat treatment in a vacuum in a quartz flask at 600°C., one gram of cellulose carbon, in contact with 25cc. of hydrogen peroxide containing 311.2cc. of available oxygen, liberated 18.65cc. of oxygen in 3 minutes. After iodine treatment, one gram of carbon, in contact with 25cc. of the hydrogen peroxide, liberated 76.4cc. of oxygen in the same time, all volumes being measured at N.T.P.

Although inulin and rice starch carbons showed considerable increases in activity after iodine treatment, potato starch and wheat starch carbons were not appreciably affected. None of the carbons investigated exhibited an increase in the initial activity comparable with that of cellulose carbon.

The present investigation on the catalytic activity of carbons derived from aromatic compounds was, therefore, undertaken in order to ascertain the differences in the initial activity (if any) exhibited by the various carbons: to study the effects of iodine treatment on the relative magnitudes of those differences; and to determine the influence (if any) of the presence of halogen, nitrogen, or sulphur in the original compound.

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[1] Firth: J. Soc. Chem. Ind. **42**, 242T (1923).

[2] Firth and Watson: J. Soc. Chem. Ind. **42**, 371T (1923).

[3] J. Chem. Soc. **123**, 1750 (1923).

Experimental

N/10-solutions of iodine in chloroform prepared as in the preceding study were used in all experiments.

An aqueous solution of hydrogen peroxide containing 321.5cc. of available oxygen (measured at N.T.P.) was employed in all cases.

Two series of experiments were carried out in which the carbon, prior to treatment with the hydrogen peroxide solution, was activated by one of the following methods:—

(I) The carbon was heated in a vacuum, in a quartz tube, at 900°C., for two hours, and then allowed to cool in a vacuum.

(II) The carbon previously treated as in (I) was allowed to stand in contact with a N/10 solution of iodine in chloroform, in the proportion of one gram of the carbon to 25cc. of the standard iodine solution. The carbon was filtered off after 24 hours, transferred to an evaporating dish, and gently heated until iodine vapours were no longer evolved. It was then digested with alcoholic potash, filtered off, washed with boiling distilled water until the filtrate remained clear on addition of silver nitrate solution, then washed with alcohol, dried, and finally heated as in (I) above, prior to treatment with the hydrogen peroxide solution.

One gram of carbon was carefully weighed out into a small flask; 25cc. of the hydrogen peroxide solution was measured out into a flat-bottomed tube, and the tube placed inside the flask. The flask was then connected with a gas burette, and the hydrogen peroxide brought into contact with the carbon by tilting the flask. Accumulation of gas in the liquid was prevented by rapid agitation.

The experiments were all carried out at 18°C.

The volumes of oxygen liberated were recorded at intervals ranging from thirty seconds to half an hour according to the velocity and stage of the reaction.

A series of blank experiments with hydrogen peroxide alone gave an average yield of 0.25cc. of oxygen in 3 hours. The volumes of oxygen recorded were corrected to N.T.P., and the Table given below shows results typical of all observed throughout the experiments.

The reaction velocity coefficients corresponding to the corrected volumes of oxygen observed at the several stages of the reaction are included in the Table, and are calculated from the equation for a unimolecular surface reaction $dx/dt = K(a-x)$ to the Naperian base, with the minute as unit of time.

The complete results of all observations for the experiments of series I and II are represented graphically in Figs. 1 and 2 respectively, whilst a summary of results with the corresponding velocity coefficients is given in the following table. (Table I).

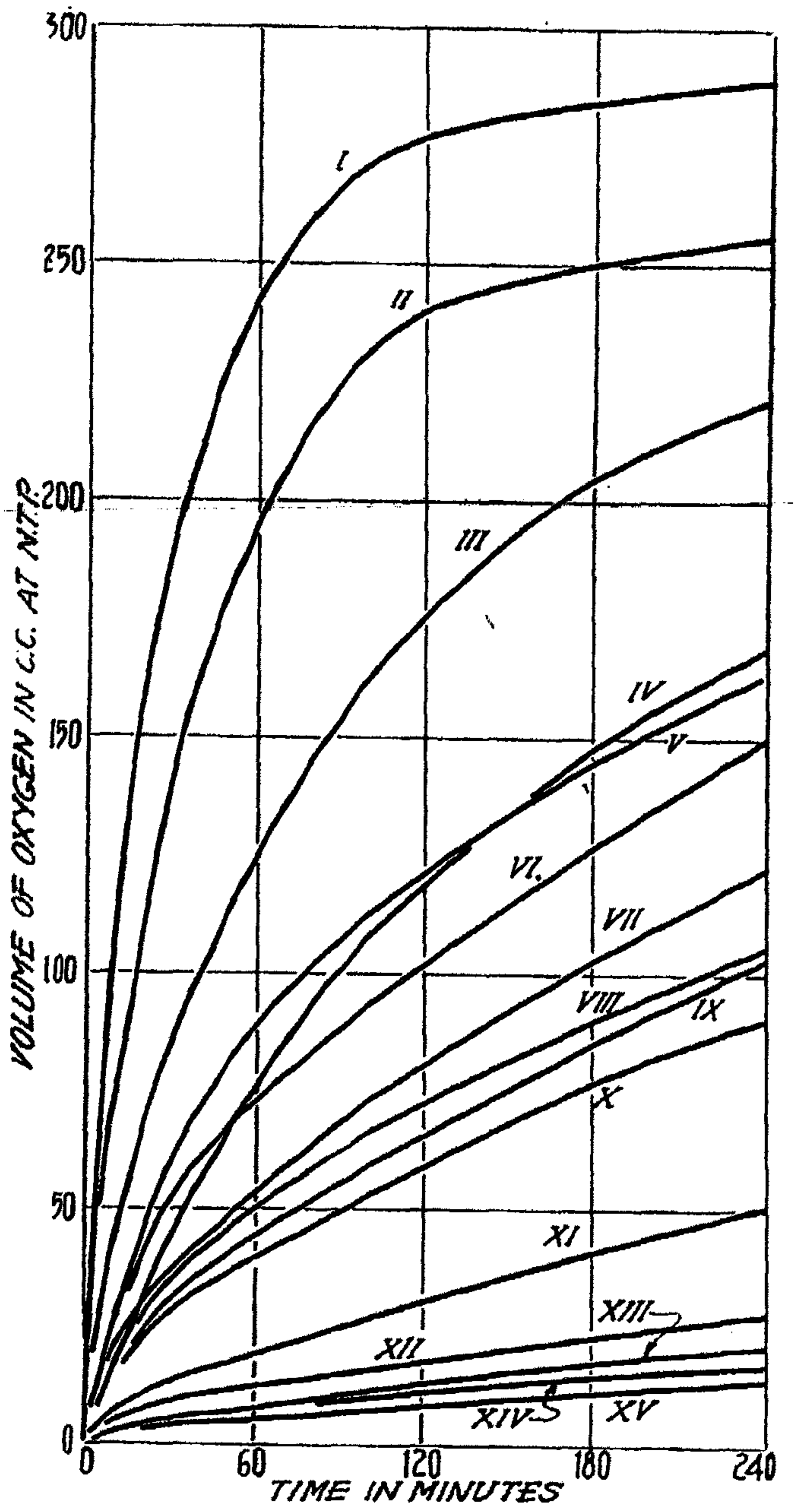

Fig. 1—Carbon not Treated with Iodine

I Metanitraniline; II diphenylamine; III thiocarbanilide; IV Paratoluidine; V anthracene; VI aniline; VII metadinitrobenzene; VIII naphthalene; IX pyridine; X alphanaphthylamine; XI monochlorobenzene; XII xylene and salicylic acid; XIII benzene, turpentine and camphor; XIV toluene and benzoic acid; XV phenol, alpha and beta-naphthol and resorcinol.

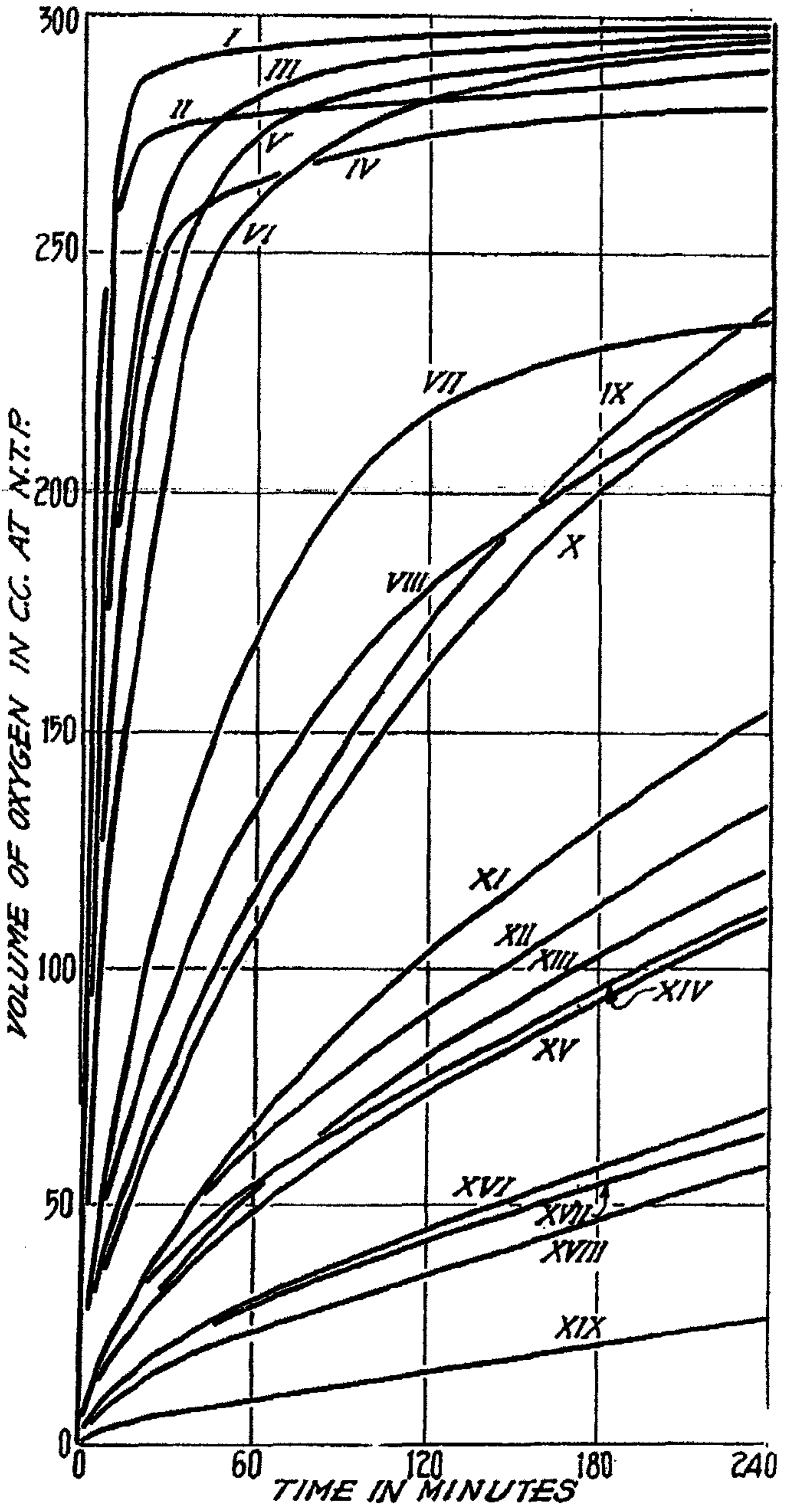

Fig. 2—Carbon Treated with Iodine

I Diphenylamine; II thiocarbanilide; III aniline; IV alphanaphthylamine; V anthracene, metanitraniline and paratoluidine; VI pyridine; VII metadinitrobenzene; VIII resorcinol; IX salicylic acid; X Turpentine; XI benzene; XII camphor; XIII benzoic acid; XIV naphthalene. XV beta-napthol; XVI monochlorobenzene; XVII phenol and alpha-naphthol; XVIII xylene; XIX toluene.

TABLE I

Time in Minutes	*Heated in vacuum at 900°* Volume of Oxygen(cc.)	K×10³	*Iodine treatment* Volume of Oxygen(cc.)	K×10³
		BENZENE		
3	0.8	0.400	10.4	4.767
6	1.5	0.350	15.4	3.567
9	1.9	0.289	19.4	3.011
30	4.5	0.203	42.6	2.060
60	7.3	0.167	67.4	1.703
120	12.5	0.143	102.7	1.393
180	17.4	0.134	131.8	1.273
240	21.8	0.127	154.4	1.184
		TOLUENE		
3	1.7	0.767	1.8	0.800
6	1.8	0.400	2.1	0.467
9	2.1	0.311	2.7	0.411
30	4.2	0.190	6.0	0.273
60	7.0	0.160	9.4	0.215
120	11.8	0.135	15.1	0.174
180	14.2	0.109	22.1	0.172
240	17.6	0.102	27.2	0.160
		XYLENE		
3	3.4	1.567	3.5	1.600
6	5.0	1.133	5.7	1.300
9	6.1	0.922	7.2	1.100
30	9.1	0.413	17.0	0.787
60	11.5	0.263	24.0	0.562
120	17.6	0.204	35.4	0.422
180	22.5	0.175	46.9	0.381
240	27.9	0.164	58.8	0.366
		NAPHTHALENE		
3	8.3	3.800	10.6	3.867
6	12.9	2.950	15.6	3.600
9	16.6	2.556	20.0	3.267
30	34.5	1.643	37.8	1.810
60	51.1	1.253	54.8	1.353
120	72.1	0.919	76.7	0.987
180	91.2	0.805	95.5	0.856
240	106.5	0.728	112.7	0.781
		ANTHRACENE		
3	10.9	5.000	73.0	37.267
6	17.5	4.050	119.0	33.450
9	22.2	3.455	143.0	28.400
30	59.2	2.947	240.9	0.030
60	88.6	2.333	274.0	13.842
120	121.2	1.713	286.1	7.985
180	145.5	1.454	291.4	5.714
240	165.6	1.310	295.8	4.572

TABLE I—Continued

Time in Minutes	*Heated in vacuum at 900°* Volume of Oxygen (cc.)	*Heated in vacuum at 900°* $K \times 10^3$	*Iodine treatment* Volume of Oxygen (cc.)	*Iodine treatment* $K \times 10^3$
		MONOCHLOROBENZENE		
3	4.5	2.033	5.2	2.367
6	5.8	1.317	7.2	1.650
9	7.3	1.111	8.8	1.333
30	12.8	0.587	19.5	0.907
60	19.5	0.453	30.9	0.732
120	30.4	0.360	44.6	0.541
180	40.2	0.322	57.6	0.476
240	51.4	0.315	70.4	0.447
		METADINITROBENZENE		
3	10.4	4.767	25.2	11.833
6	14.8	3.417	40.7	9.800
9	18.9	2.922	55.2	9.089
30	37.1	1.777	121.8	6.890
60	53.5	1.318	170.6	5.477
120	80.6	1.045	216.9	4.064
180	102.3	0.924	229.5	3.019
240	122.8	0.870	236.2	2.401
		ANILINE		
3	12.3	5.633	99.1	53.333
6	19.7	4.583	148.3	44.783
9	24.8	3.878	178.1	38.967
30	50.1	2.453	264.0	24.917
60	72.7	1.855	283.0	15.362
120	101.3	1.370	291.5	8.584
180	127.0	1.213	294.9	6.013
240	149.9	1.136	296.3	4.608
		PARATOLUIDINE		
3	6.1	2.767	87.9	46.233
6	9.8	2.233	134.5	39.233
9	13.9	2.133	166.9	35.333
30	41.5	2.000	246.3	21.033
60	75.9	1.948	273.6	13.782
120	118.9	1.671	286.8	8.058
180	148.1	1.490	291.3	5.707
240	168.8	1.348	293.6	4.423
		ALPHANAPHTHYLAMINE		
3	6.9	3.167	91.8	48.667
6	10.5	2.400	140.1	41.433
9	13.6	2.089	175.9	38.222
30	28.5	1.343	251.6	24.327
60	39.8	0.957	264.4	12.510
120	59.9	0.747	275.5	7.037
180	77.4	0.664	279.4	4.905
240	92.9	0.617	281.5	3.771

TABLE I—Continued

Time in Minutes	*Heated in vacuum at 900°* Volume of Oxygen(cc.)	$K \times 10^3$	*Iodine treatment* Volume of Oxygen(cc.)	$K \times 10^3$
		METANITRANILINE		
3	63.9	32.100	75.0	38.467
6	88.9	23.433	114.6	31.900
9	106.9	19.511	147.0	29.489
30	193.0	13.277	246.0	20.977
60	242.8	10.187	276.2	14.185
120	277.3	7.182	286.3	8.006
180	282.9	5.114	289.9	5.597
240	286.7	4.023	293.4	4.410
		DIPHENYLAMINE		
3	34.4	16.367	130.9	75.700
6	50.8	12.450	180.7	59.883
9	67.7	11.411	224.8	57.978
30	142.0	8.437	289.4	33.357
60	196.9	5.862	293.8	17.745
120	239.5	4.945	295.9	9.158
180	250.0	3.627	297.0	6.211
240	255.9	2.876	298.5	4.773
		THIOCARBANILIDE		
3	17.8	8.267	149.4	90.500
6	29.2	6.900	208.7	75.833
9	38.9	6.233	237.9	65.000
30	84.9	4.440	275.7	28.210
60	126.2	3.610	278.6	14.578
120	175.7	2.863	281.5	7.543
180	294.7	2.443	284.7	5.230
240	221.8	2.119	289.0	4.147
		PHENOL		
3	1.3	0.600	3.6	1.633
6	1.5	0.350	6.0	1.367
9	1.7	0.256	7.3	1.111
30	3.0	0.137	20.0	0.930
60	4.8	0.108	29.8	0.705
120	7.4	0.085	44.0	0.533
180	11.0	0.084	55.9	0.461
240	14.1	0.081	66.0	0.416
		ALPHANAPHTHOL		
3	1.1	0.533	3.8	1.700
6	1.6	0.367	5.8	1.317
9	2.1	0.311	7.1	1.078
30	3.4	0.157	15.7	0.727
60	5.0	0.113	25.3	0.593
120	7.5	0.086	40.1	0.483
180	10.4	0.079	55.1	0.453
240	13.0	0.075	68.4	0.433

TABLE I—Continued

	Heated in vacuum at 900°		*Iodine treatment*	
Time in Minutes	Volume of Oxygen(cc.)	$K \times 10^3$	Volume of Oxygen(cc.)	$K \times 10^3$
		BETANAPHTHOL		
3	1.2	0.567	6.7	3.067
6	1.5	0.350	11.5	2.633
9	1.8	0.267	15.4	2.378
30	2.7	0.123	33.0	1.567
60	4.2	0.095	49.9	1.222
120	7.2	0.083	75.6	0.970
180	10.2	0.078	94.1	0.830
240	13.1	0.075	111.8	0.773
		RESORCINOL		
3	1.1	0.533	24.6	11.533
6	1.6	0.367	39.0	0.367
9	2.0	0.300	49.4	9.044
30	3.0	0.137	96.3	5.153
60	4.6	0.105	134.3	3.915
120	7.4	0.085	178.3	2.928
180	10.4	0.079	205.3	2.455
240	13.1	0.075	226.0	2.197
		BENZOIC ACID		
3	1.0	0.467	7.7	3.533
6	1.9	0.433	12.4	2.850
9	2.3	0.344	16.3	2.544
30	4.3	0.193	33.9	1.613
60	5.8	0.132	53.7	1.323
120	9.3	0.106	81.1	1.053
180	12.5	0.096	102.1	0.922
240	15.8	0.091	121.0	0.855
		SALICYLIC ACID		
3	1.5	0.700	19.0	8.833
6	2.0	0.450	30.4	7.200
9	2.6	0.400	39.1	6.267
30	5.7	0.260	79.1	4.090
60	9.3	0.212	116.2	3.247
120	15.9	0.183	172.1	2.773
180	22.7	0.177	211.0	2.577
240	28.2	0.166	239.7	2.477
		TURPENTINE		
3	2.2	1.000	20.4	9.500
6	2.5	0.567	30.3	7.167
9	3.5	0.533	36.5	5.822
30	4.8	0.217	71.7	3.653
60	7.0	0.160	108.4	2.977
120	12.0	0.138	162.3	2.544
180	15.1	0.116	200.7	2.362
240	19.9	0.115	225.0	2.178

Table I—Continued

Time in Minutes	*Heated in vacuum at 900°* Volume of Oxygen(cc.)	$K \times 10^3$	*Iodine treatment* Volume of Oxygen(cc.)	$K \times 10^3$
		CAMPHOR		
3	2.1	0.933	10.5	4.800
6	3.3	0.750	16.4	3.800
9	3.7	0.556	21.1	3.278
30	7.0	0.320	43.7	2.113
60	9.3	0.212	63.8	1.602
120	14.4	0.167	90.6	1.198
180	18.6	0.144	112.7	1.041
240	23.0	0.135	134.3	0.979
		PYRIDINE		
3	6.6	3.033	49.2	24.033
6	10.4	2.383	82.8	21.550
9	14.0	2.156	113.2	20.944
30	30.9	1.463	214.2	15.887
60	44.4	1.075	259.7	11.937
120	65.7	0.828	282.0	7.588
180	86.4	0.755	288.2	5.471
240	104.0	0.707	292.8	4.372

Discussion of Results

After heating in a vacuum for two hours, at 900°C., the different carbons exhibit a graded variation in activity relative to hydrogen peroxide. This is most marked in the case of metanitraniline and diphenylamine carbons, and least for the carbons derived from phenol, alpha-, and beta-naphthol, and resorcinol, these showing approximately similar activity. Cf the carbons obtained from aromatic hydrocarbons, that from anthracene shows the highest activity, and those from benzene and turpentine the least.

Pyridine carbon shows an activity considerably higher than benzene carbon, and only slightly less than that of naphthalene carbon. The activity of monochlorobenzene carbon is higher than benzene carbon, and the same is true of thiocarbanilide carbon with respect to carbon from aniline.

An interesting feature of the results is that, in addition to the cases already mentioned, carbons derived from the following pairs of substances show similar catalytic activity:—(a) toluene and benzoic acid, (b) xylene and salicylic acid, (c) anthracene and paratoluidine, (d) turpentine and camphor.

Whilst, in this series of experiments, carbons derived from amine bases show the highest activity, and those from phenolic substances the least activity, there is not sufficient evidence to show to what extent (if any) the activity is enhanced by nitrogen on the one hand, and diminished by oxygen on the other; or, indeed, whether any influence on the catalytic activity of the carbons is to be attributed to the elements themselves, or to the amino-, and hydroxyl-groups in which they occur.

The results of the second series of experiments indicate that previous sorption of iodine produces a marked increase in the activity of all the carbons, with the exception of toluene and naphthalene carbons. Very considerable increases in activity are exhibited by the carbons obtained from aniline, anthracene, paratoluidine, thiocarbanilide, and alphanaphthylamine. Of the carbons derived from phenolic substances, that from resorcinol shows the highest activity, while phenol, and alpha-naphthol carbons show the least activity. Salicylic acid carbon shows a much higher activity than benzoic acid carbon, and the same may be said of turpentine carbon with reference to camphor carbon, and of benzene carbon with respect to monochlorobenzene carbon.

With the exception of anthracene carbon, the carbons showing the highest catalytic activity are derived from substances containing basic nitrogen, with sulphur in addition, in the case of carbon from thiocarbanilide.

From a study of the catalytic decomposition of hydrogen peroxide by blood charcoal, Firth and Watson[1] showed that the effect of the various methods of activation is confined to the initial reaction.

The blood charcoal, purified by digestion for a month with aqua regia, and subsequent washing with boiling distilled water until the filtrate showed no indication of iron with potassium sulphocyanide solution, was activated by one of the following methods:—(I) by heat treatment at 600°C.;(II) by heat treatment at 900°C.: (III) by heat treatment as in (I), iodine treatment, and then heat treatment as in (I): (IV) by heat treatment as in (II), iodine treatment, and then heat treatment as in (II). In each experiment, 25cc. of hydrogen peroxide solution containing 242.5cc. of available oxygen (measured at N.T.P.) was used with 0.25 gram of the activated charcoal as catalyst.

An examination of the results obtained showed that during the first thirty seconds, the percentage of hydrogen peroxide decomposed by the charcoals activated by methods I., II., III., and IV., respectively, was 9.32, 9.68, 17.1, and 25.13, whilst after twelve minutes the values were very similar in all cases. The corresponding velocity constants for the first thirty seconds were 85.00, 96.40, 162.60, and 258.80, respectively. After twelve minutes they were 37.94, 41.33, 41.51, and 42.13, whilst after 60 minutes, when 74.5 per cent. of the hydrogen peroxide had been decomposed by each charcoal, they were reduced to approximately the same value, the respective constants being 9.33, 9.56, 9.60, and 9.91.

The velocity coefficients for unactivated blood charcoal were 10.2 for thirty seconds, and 9.4 for one minute.

From these results the authors concluded that the extent of the decomposition is not determined by the initial activity, because charcoals of widely different initial activities approach similar values after about thirty minutes.

The authors, therefore, put forward the view that the catalytic activity of the blood charcoal is of two types, one, a very rapid activity which decays

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[1] Trans. Faraday Soc. 19 III, No. 57 (1924).

after a few minutes, and the other a much slower activity which persists for a much longer period. Both forms may be increased by activation methods. These two types of activity have been termed, alpha, and beta activity, respectively. Unactivated blood charcoal does not show alpha activity. Provided that the alpha activity is not sufficient to bring about complete decomposition of a hydrogen peroxide solution of given strength, it is the beta activity which determines the limit of decomposition.

In the present investigation, a study of the results obtained from the experiments of series II shows that in their activity towards hydrogen peroxide the various carbons may be arranged in three groups:—(a) carbons exhibiting a rapid initial, or alpha activity, followed by a very slow beta activity: (b) carbons showing little or no alpha activity, and whose activity is almost entirely of the beta type: (c) carbons possessing the two types of activity without the pronounced demarkation between the alpha and beta activities, as exhibited in (a).

With the exception of metanitraniline, naphthalene, and toluene carbons, the combined effect of the alpha and beta types of activity is to increase the percentage decomposition of the hydrogen peroxide solution, and this is clearly shown by a comparison of the velocity coefficients for the carbons activated by the methods employed in the experiments of series I and II. In no case, however, is there complete decomposition of the hydrogen peroxide in a reasonable time.

Summary

1. The carbons derived from various aromatic compounds show a graded activity relative to hydrogen peroxide when activated by heat treatment in a vacuum, at 900°C.

2. The activity of the majority of the carbons is considerably increased by previous sorption of iodine from chloroform solution.

3. The carbons exhibiting the highest initial activity are, in the majority of cases, derived from compounds containing basic nitrogen.

University College,
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PRELIMINARY EXPERIMENTS ON FEATHER PIGMENTS[1]

BY WILDER D. BANCROFT

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The experiments described in this paper were made by Mr. J. R. Adams. The pigment in the feathers of the Cock of the Rock was extracted with alcohol and some dyeing tests were made with the yellow solution. In a slightly acid solution wool was dyed yellow; in a neutral solution wool was dyed a paler yellow; and in a slightly alkaline solution no perceivable color was imparted to the wool. Silk was also dyed yellow in a slightly acid solution, while cotton was not dyed at all. Alumina from aluminum was colored yellow. The pigment therefore behaves like an acid dye. The pigment can also be extracted from these feathers by means of a hot sodium carbonate solution.

In the next set of experiments, the skin of a cardinal was obtained from Professor Arthur A. Allen. The feathers were removed and washed with water to remove such dirt as could be removed. Treatment with a sodium oleate solution removed the color completely, leaving a perfectly white feather; but no good way was found to separate the dye from the sodium oleate solution. If acid is added, the color is thrown down as a reddish brown precipitate. The feathers were therefore extracted with alcohol, and a yellow solution was obtained having apparently just the same color as the corresponding extract of the feathers of the Cock of the Rock. The pigment comes out readily at first and then more slowly and the feathers always retained a certain reddish tinge. This residual color seems to be the characteristic pink, which differentiates the cardinal feathers from those of the Cock of the Rock. The dyeing experiments came out exactly like the preceding ones.

Diffusion experiments with the two pigments in acid, basic, and neutral solutions gave the same results, and it was also found that the pigment could be extracted from the cardinal feathers with a hot sodium carbonate solution. The absorption bands were determined roughly for each solution spectroscopically and the solutions seemed practically identical. Some experiments were also made as to the fading of the colors on exposure to light. Feathers from the Cock of the Rock and from the cardinal were placed in a Fadeometer. The feathers from the Cock of the Rock changed in a few hours to yellow and then to white. The feathers from the cardinal took a much longer time to fade but the change was to a dark yellow and then to white.

In both cases the solutions leave an orange-red residue if allowed to evaporate at room temperature. It seems probable therefore that the pigment in the feathers of the Cock of the Rock is substantially identical with that in the feathers of the cardinal, though it is not proved that the identity may be only in the extracted pigments.

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[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

The question arises, however, why a red pigment should dye yellow. There are two possible answers. The red pigment may be decomposed into a yellow pigment during extraction, or the red and yellow pigments may be identical chemically, the difference being purely a question of aggregation. We know that ferric oxide (rouge) and potassium ferricyanide are red in coarse crystals and are yellow when very finely divided. It is not possible at present to decide between these two hypotheses; but it is interesting to note that an orange-red precipitate was obtained when the solutions evaporated, which should not be the case if the red pigment had decomposed.

When the red feathers of the red-headed woodpecker are extracted with alcohol for ten hours, they change to a light shade of gold, and the red feathers of the red-winged blackbird change to yellow under the same conditions, after which there is practically no further extraction. In the case of the fruit pigeon, the yellow was extracted completely in ten hours; but the red was not affected at all. The red of the scarlet tanager is extremely resistant to alcohol and so is the brown of the canvas-back duck.

It seems probable that there are at least two groups of red or yellow colors, those which are extremely resistant to alcohol and those which are not. There is no doubt as to the apparent difference between them; but it is of course possible that there is some other substance present in the feathers in one set of cases which acts as a mordant and retards extraction. There seems also to be a very distinct relation between the resistance to extraction by alcohol and the resistance to fading in light. The brown of the canvas-back duck and the red of the scarlet tanager are practically fast to light. The yellow Toucan feathers bleach in six hours in the Fadeometer and the red changes to a brown which bleaches on a longer exposure. Both colors come out readily with alcohol. With the fruit pigeon the yellow faded rapidly while the red did not. The feathers of the Blue and Yellow Macaw were exposed in the Fadeometer for 105 hours, at which time the orange had changed to a yellow which was not removed by further exposure. On extraction the orange changed to a lemon-yellow, which could not be extracted. On the other hand the yellow of the golden pheasant can be extracted in about sixteen hours and fades in less than fifteen hours.

If one wished to make three classes, one could take the toucan, golden pheasant, and cardinal as having pigments which fade readily and which are easily extracted with alcohol. The feathers from the fruit pigeon, the blue and yellow macaw, and the yellow-headed Amazon parrot fade slowly and the pigment can only be extracted slowly. The black of the crow, the brown of the canvas-back duck, and the red of the scarlet tanager do not fade at all and are almost impossible to extract.

It is well known that the reds of the bronze-headed trogon and of the flamingo are extremely fugitive to light. No experiments have been done with these to determine resistance to extraction by alcohol.

Lloyd-Jones,[1] is evidently of the opinion that reds and yellows in feathers are identical chemically. "Among self-colored birds the colors red and yellow are perfectly distinct. Even the lightest reds and the darkest yellows are easily placed in their proper class. In appearance these colors bear the relation to each other of dilute and intense conditions of the same pigment material. That yellow is a dilute condition can be demonstrated by even a hasty examination of the feathers, and the fact is farther borne out to the degree of certainty by a comparative chemical study of the two different kinds of feathers. Microscopically, the 'yellow' pigment is seen to be far more sparsely distributed than in reds. Often under strong light the pigment in the barbules is almost imperceptible....

"The crucial difference between yellow and red, however, has not yet been mentioned. It is concerned with the nature and form of the pigment granules. As shown above, the pigment in reds exists as distinct, clear-cut, spherical granules, typically 0.3μ in diameter. No such spheres have ever been found in yellow feathers, in the course of my work. The pigment exists as irregular formless clumps, or agglomerations. These blotches of pigment appear finely granular in nature; but are so fine that discrete particles are beyond the limits of a 18 mm oil immersion objective. This difference between reds and yellows is sharp and is constant. When minute patches of reddish pigment are present on a dun, black, or white feather, it is frequently difficult or impossible by gross examination to classify the color as red or yellow; but miscropic study of such areas serves unfailingly to distinguish the colors by virtue of the morphological difference above cited."

On a later page Lloyd-Jones draws the following conclusions:—

1. There is a red-brown pigment substance which produces the colors red and yellow in tumbler pigeons.

2. In red birds this pigment always exists as spherical granules, which are in 'typical red' about 0.3μ in diameter; but in 'plum color' they are 2.0μ or more in diameter.

3. In yellows the pigment is so finely divided that its granule form cannot be determined.

It is possible that these generalizations apply only to the material studied by Lloyd-Jones; but they are certainly interesting and they may turn out to be quite general, though it is rather to be expected that different yellows—and consequently reds—will show up differently under the microscope.

The general conclusions of this paper are as follows:—

1. Some reds and yellows are very resistant to extraction with alcohol while others are not. Those reds and yellows which are not easily extracted by alcohol are pretty fast to light and the converse seems also to be true.

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[1] J. Exp. Zoology, **18**, 464 (1915).

2. When extracted by alcohol, the red and the yellow pigments give yellow solutions which are apparently identical. It is not known whether the red pigment is converted into a yellow one at the time of extraction or whether the red pigment differs structurally from the yellow one in being coarser, just as we know is the case with red and yellow mercuric oxide, ferric oxide, and potassium ferricyanide.

3. The extracted pigment behaves like an acid dye because it does not dye cotton direct and dyes wool most strongly in an acid bath and least strongly (or not at all) in an alkaline bath. It is also taken up to some extent by alumina

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THE CALCULATION OF GASEOUS EQUILIBRIUM CONSTANTS

BY SIDNEY WALTER SAUNDERS

Introduction

The object of this paper is to analyse the existing data on the molecular heats of gases, heats of reaction, chemical and equilibrium constants for well known reactions involving carbon, hydrogen, oxygen and nitrogen, and to come to a decision as to the best values for these constants. From these data, it should then be possible to calculate the equilibrium constants of reactions for which experimental data are scanty, and for reactions taking place at high temperatures. The conclusions reached should be of practical value for the study of the gas reactions occurring in producer and coal-gas manufacture, in the detonation of high explosives, etc. The calculations are confined to the key reactions between substances containing carbon, hydrogen, oxygen and nitrogen.

Calculation of Gaseous Equilibrium Constants

There are two general methods for the theoretical calculation of equilibrium constants.

The first is by integration of the van't Hoff equation

$$\frac{d}{dT}(\ln K_p) = -\frac{Q_p}{RT^2}$$

where K_p is the equilibrium constant expressed in partial pressures, and Q_p is the heat evolved in the reaction from left to right at the temperature T° K, and the determination of the integration constant thereby introduced. Nernst found that, making certain assumptions, this constant was the sum of values characteristic of each substance participating in the reaction, to which he gave the name chemical constant. These chemical constants can be evaluated from vapour pressure measurements and from other physical data in a semi empirical manner. Other workers determine the integration constant from one or more determinations of the equilibrium constant, this method being employed by G. N. Lewis and his co-workers[1], for the calculation of free energies.

The second method is based on the fact that

$$K = k_1/k_2$$

Where K is the equilibrium constant, and k_1 and k_2 are the velocity constants of the direct and reverse reactions, and thus obviates the need for the determination of any integration constant. Unfortunately, theoretical methods for the calculation of the velocity constant are uncertain, and in most cases,

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[1] See Lewis and Randall: "Thermodynamics" (1922).

data are wanting to test them. On this basis, and with some assumptions, Dushman[1] obtained equations for the calculation of equilibrium constants, which give approximate values, although they "lay no claim to strict validity".

Equation for the Equilibrium Constant

Consider the reaction

$$n_1 a_1 + n_2 a_2 + \ldots + \nu_1 A_1 + \nu_2 A_2 + \ldots \rightleftarrows n_1{}^1 a^1{}_1 + n_2{}^1 a_2{}^1 + \ldots + \nu^1{}_1 A^1{}_1 + \nu_2{}^1 A_2{}^1 + \ldots \qquad (1)$$

where *n* and *a* refer to solids, and ν and A to gases.

Then if Q_p^T is the heat evolved at T° K and at constant pressure in the reaction from left to right, we know that

$$dQp = \int (\Sigma n + \Sigma \nu) \cdot C_p^T dT \qquad (2)$$

where C_p^T is the true molecular heat of each substance at T° K, and where $(\Sigma n + \Sigma \nu) C_p^T$ refers to the algebraic sum (reactants positive, and resultants negative), of the number of mols of each substance concerned in the equation multiplied by its C_p^T.

$$\text{Let } C_p^T = \alpha + 2\beta T + 3\gamma T^2 + \ldots \qquad (3)$$

where α, β and γ are constants.

Then the mean molecular heat at constant pressure between 0°K and T°K is given by

$$C_p^{0.T.} = \alpha + \beta T + \gamma T^2 + \ldots \qquad (4)$$

For solids, $\alpha, \beta, \gamma, \ldots$ are replaced by a, b, c, ...

By integrating equation (2) we get

$$Q_p^T = (\Sigma na + \Sigma \nu\alpha)T + (\Sigma nb + \Sigma \nu\beta)T^2 + (\Sigma nc + \Sigma \nu\gamma)T^3 + \ldots + Q_0 \qquad (5)$$

where the integration constant, Q_0, is the value of Q_p at 0° K.

$$\text{Now, if } K_p = \frac{p_{A^1_1}^{\nu^1_1} \cdot p_{A^1_2}^{\nu^1_2} \cdot \ldots}{p_{A^1}^{\nu^1} \cdot p_{A_2}^{\nu_2} \cdot \ldots} \qquad (6)$$

where p_A .. is the partial pressure of A ...
the van't Hoff Isochore states that

$$\frac{d}{dT} \cdot \ln K_p = - \frac{Q_p}{RT^2} \qquad (7)$$

On integration,

$$\ln K_p = \frac{Q_0}{RT} - \frac{(\Sigma ua + \Sigma \nu\alpha)}{R} \ln T - \frac{(\Sigma ub + \Sigma \nu\beta)}{R} T - \frac{(\Sigma uc + \Sigma \nu\gamma)}{2R} T^2 - \ldots - \text{Const.} \qquad (8)$$

On applying the Nernst theorem, this Constant = $\Sigma \nu C$ (9)

where $\Sigma \nu C$ is the algebraic sum of the so called "Conventional Chemical Constants" of Nernst. The numerical calculation of this constant for each substance involves assumptions with regard to molecular heats of gases and

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[1] J. Am. Chem. Soc. 43, 397 (1921).

of latent heats of vaporisation at O° K. There are, however, approximate empirical methods for its calculation, which are based on critical data, boiling point, and the latent heat of vaporisation at the boiling point.

Equation (8) cannot be used, since Q_0, a, b, c, α, β, γ, . . . are unknown; hence, any calculations for the determination of $\ln K_p$ must, because of insufficient data, be empirical. However, by taking the experimental results for $C_p^{273.T}$, and extrapolating to O° K, we can get an approximate expression for $C_p^O \cdot T$.

Let this equation be

$$C^1{}_p{}^{O.T.} = \alpha^1 + \beta^1 T + \gamma^1 T^2, \text{ for gases,} \qquad (10)$$

and

$$C^1{}_p{}^{O.T.} = a^1 + b^1 T + c^1 T^2, \text{ for solids.} \qquad (11)$$

Then, as before,

$$Q_p^T = (\Sigma u a^1 + \Sigma \nu \alpha^1)T + (\Sigma u b^1 + \Sigma \nu \beta^1)T^2 + (\Sigma u c^1 + \Sigma \nu \gamma^1)T^3 + Q^1{}_0 \qquad (12)$$

where $Q^1{}_0$ is an integration constant.

Equation (8) then becomes, when combined with equation (9),

$$\ln K^1{}_p = \frac{Q^1{}_0}{RT} - \frac{(\Sigma u a^1 + \Sigma \nu \alpha^1)}{R} \ln T - \frac{(\Sigma u b^1 + \Sigma \nu \beta^1)}{R} \cdot T - \frac{(\Sigma u c^1 + \Sigma \nu \gamma^1)}{2R} T^2 - \Sigma \nu C. \qquad (13)$$

The justification for this procedure can be shown as follows.

If we assume for each substance, $\alpha^1 = x \cdot \alpha$ and $\beta^1 = y \cdot \beta$ where x and y are constants, it can be shown that, neglecting the γ^1 term, whose weight in equation (13) is small, the difference between the true $\ln K_p$ and the value given by equation (13), i.e.

$$\ln K_p - \ln K^1{}_p = \left(1 - \frac{1}{x}\right)\left(\frac{\Sigma u a^1 + \Sigma \nu \alpha}{R}\right)\left(\frac{273}{T} + \mathrm{lu} T\right) + \left(1 - \frac{1}{y}\right)\left(\frac{\Sigma u b^1 + \Sigma \nu \beta^1}{R}\right)\left(T + \frac{273^2}{T}\right) \qquad (14)$$

(The value of $Q^1{}_0$ is deduced from the value of Q_p at 273°K).
We know that $\alpha^1 > \alpha$ and, since the rise in the molecular heat from O°K to T°K, i.e. C_p^O to C_p^T must be greater than $C^1{}_p^O$ to C_p^T, $\beta^1 < \beta$.

$$\therefore \quad \left(1 - \frac{1}{x}\right) \text{ is } + \text{ ve, and } \left(1 - \frac{1}{y}\right) \text{ is } - \text{ ve .}$$

The two terms on the right hand side of equation (14) thus tend to counterbalance, but the actual difference cannot be found, since α and β are unknown. This difference is certainly very small, and we are thus justified in using the Nernst chemical constants together with the empirical molecular heat equations for the approximate calculation of $\ln K_p$.

Except in the case of nitric oxide the use of these constants gave good results.

In cases where the data are not sufficiently accurate, the approximate Nernst equation

$$\ln K_p = \frac{Q_0^1}{RT} - \frac{\Sigma\nu \times 1.75}{R} \ln T - \frac{(\Sigma u b^1 + \Sigma\nu\beta^1)}{R} \cdot T - \frac{(\Sigma u C^1 + \Sigma\nu\gamma^1)}{2R}$$

$$T^2 - \Sigma\nu C. \qquad (15)$$

is used, in which the assumption that $C_p^O = 3.5 + 1.5 \times n$ (16)
is made. (n = the number of atoms in the molecule of the substance.)

Where there are still less data, the Nernst method for the determination of the b¹ + β¹ term is used:—

$$\Sigma u b^1 + \Sigma\nu\beta^1 = \frac{\Sigma\nu C_{p\,\text{Solid.}}^{\text{True}} + \Sigma\nu C_p^{\text{True}} - \Sigma\nu \times 3.5}{2T} \qquad (17)$$

where T is any temperature (preferably in the middle of the region for which the equation is used) corresponding to C_p. This is substituted in equation (15), and the $c^1 + \gamma^1$ term neglected.

The corresponding value of Q^1_0 is given by

$$Q^1_0 = Q_p^T - \Sigma\nu \times 3.5 - (\Sigma u b^1 + \Sigma\nu\beta^1)T^2 \qquad (18)$$

The Molecular Heats of Gases

The molecular heats of gases are usually given in the literature as the mean between 273°K and T °K at constant pressure. In cases where they are not, they were converted to these conditions. These values were plotted against T °K, a smooth curve drawn through the points thus obtained and the curve produced backwards to 0°K

An equation of the form

$$C_p^{273.T.} = d + eT + fT^2$$

where d, e and f are constants, was then found to fit it. The T^2 term was never exceeded, since the experimental data were never sufficiently accurate. In order to derive an approximate value for $C_p{}^{1\,O.T.}$, it was assumed that, putting T = 0,

$$C^1{}_p{}^{0.273.} = d.$$

The molecular heats of gases decrease rapidly below about 200°K but except for hydrogen, there is a lack of data so that more accurate equations cannot be derived. $C^1{}_p{}^{O.T.}$ is thus a fictitious value greater than the true mean molecular heat at constant pressure.

It can be shown that

$$C^1{}_p{}^{O.T.} = (d - 273 \cdot e) + T(e - 273 \cdot f) + T^2 \cdot f$$
$$\equiv \alpha^1 + \beta^1 T + \gamma^1 T^2$$

which is the form of equation used in the determination of the equilibrium constants.

The results from the data collected will now be given.

Hydrogen

The curve $C_p^{273.T.}/T$ rises rapidly from 5 to 6.76 as the temperature changes from 50°K to 273°K, when it becomes linear, so that no equation of the proposed, or of any simple type, will fit it. The equations proposed hold above 273°K. They are:—

$C_p^{O.T.} = 6.52 + 0.00044\ T$

$C_p^{OC.tC.} = 6.76 + 0.00044t$

Equations given in the literature are:—

$C_p^{OC.tC.} = 6.70 + 0.00045t$ . . . . Pier[1].

$C_p^{OC.tC.} = 6.60 + 0.000532\ t$ . . . . Holborn and Henning[2].

$C_p^{OC.tC.} = 6.85 + 0.00064\ t$ . . . . Crofts[3].

$C_p^{OT.} = 6.50 + 0.00045\ T$ . . . . Lewis and Randall[4].

Nitrogen, Nitric Oxide, Carbon Monoxide and Oxygen

The curve for nitrogen is linear at all temperatures. As far as experimental evidence goes, nitric oxide, carbon monoxide and oxygen have the same molecular heat as nitrogen.

The equations selected are:—

$C_p^{O.T.} = 6.41 + 0.000523\ T.$

$C_p^{OC.tC.} = 6.69 + 0.000523\ t.$

Equations given in the literature are:—

$C_p^{OC.tC} = 6.90 + 0.00045\ t$ . . . . Pier[5].

$C_p^{OC.tC.} = 6.60 + 0.000532\ t$ . . . . Holborn and Henning[6].

$C_p^{16C.tC.} = 6.70 + 0.0004\ t$ . . . . Crofts [7].

$C_p^{O.T.} \doteq 6.775 + 0.00021\ T$ . . . . Dixon, Camphell and Parker[8].

$C_p^{O.T.} = 6.50 + 0.0005\ T$ . . . . Lewis and Randall[9].

Water

At high temperatures, the values given by Bjerrum and Pier, are not very concordant. The following equations are chosen.

$C_p^{O.T.} = 7.67 + 0.000394\ T + 3.167 \times 10^{-7}\ T^2.$

$C_p^{OC.tC.} = 7.95 + 0.000652\ t + 3.167 \times 10^{-7}\ T^2.$

Equations given in the literature are:—

$C_p^{100.C\ tC.} = 8.429 - 0.000302\ t + 7.92 \times 10^{-7}\ t^2$ . . Holborn and Henning[2]

$C_p^{OC.tC.} = 8.065 + 0.0005\ t + 2 \times 10^{-10}\ t^3$ . . . . Pier[1].

$C_p^{O.T.} = 8.81 - 0.00095\ T + 7.4 \times 10^{-7}\ T^2$ . . . . Lewis and Randall[6].

The Lewis and Randall equation gives a minimum value for $C_p^{O.T.}$ of 8.5 at 670°K.

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[1] Z Elektrochem. 15, 536 (1909).

[2] Ann. Physik, (4) 23, 809 (1907).

[3] J. Chem. Soc. 1071, 290 (1915).

[4] J. Am. Chem. Soc. 34, 1128, (1912), and "Thermodynamics," p. 80 (1922)

[5] l.c.

[6] l.c.

[7] l.c.

[8] Proc. Roy. Soc. 100A, 1 (1921).

[9] l.c.

Carbon Dioxide

The molecular heat of carbon dioxide falls off rather suddenly below room temperatures.

The equations selected are:—
$C_p^{O.T.} = 7.34 + 0.003397\ T - 6.10 \times 10^{-7}\ T^2$
$C_p^{OC.tC.} = 9.05 + 0.002896\ t - 6.10 \times 10^{-7}\ t^2$
Equations given in the literatures are:—
$C_p^{OC.tC.} = 8.80 + 3.3 \times 10^{-3} t - 0.95 \times 10^{-6} t^2 + 0.1 \times 10^{-9} t^3$....Pier[1].
$C_p^{OC.tC.} = 8.859 + 0.003265\ t - 7.92 \times 10^{-7} t^2$....Holborn and Henning[2].
$C_p^{O.T.} = 8.30 + 0.001025\ T + 2.3 \times 10^{-7}\ T^2$....Dixon and others[3].
$C_p^{O.T.} = 7.0 + 0.00355\ T - 6.2 \times 10^{-7}\ T^2$....Lewis and Randall[4].

Carbon

The form of carbon selected for these calculations is graphite. There are numerous values given in the literature for the true atomic heat at constant pressure up to 1000°K, but beyond this, the figures given by Violle had to be used. The C_p^T curve rises slowly from about 0°K to 100°K, then rapidly up to about 1000°K, and beyond this, the atomic heat remains nearly constant. No equation of the ordinary type will fit this unless many more terms are added.

The equations selected are: -
$C_p^{O.T.} = 1.28 + 0.00209\ T - 2.23 \times 10^{-7}\ T^2$
$C_p^{OC.tC.} = 2.37 + 0.00191\ t - 2.23\ 10^{-7}\ t^2$
Lewis and Randall[5] give for graphite
$C_p^{O.T.} = 1.1 + 0.0024\ T - 4.0\ 10^{-7}\ T^2$.

At ordinary temperatures, the atomic heat of graphite is 1.9 and of amorphous carbon 2.6. The above equations give 2.4.

For graphite, Dewar gave $C_p^{OC.1040C.} = 3.72$. Calculated from above = 4.12
" " Violle " $^{-2000C.}$ 5.70 " " 5.30
" " " " $^{-3000C.}$ 6.39 " " 6.09

Other Gases

Hydrocyanic Acid. There are no data for the molecular heat of hydrocyanic acid, but Ingold and Usherwood[6] found the ratio Cp/Cv by Kundt's method, at temperatures from 65°C to 210°C, so that an approximate value for Cp can be calculated. At the mean temperature of their experiments, 400°K, the molecular heat of hydrocyanic acid is 0.7 higher than that of

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[1] Z. Elektrochem. 16, 897 (1910).
[2] l.c.
[3] l.c.
[4] l.c.
[5] "Thermodynamics", p. 569, (1922).
[6] J. Chem. Soc., 121- 1604 (1922).

water. As both liquid water and hydrocyanic acid are strongly associated, their molecular heats will probably be very similar. Assuming then, that

$C^{O.T.}_{pH_2O} + 0.7 = C^{O.T.}_{pHCN}$ „ we get for $C^{O.T.}_{pHCN}$

$C_p^{O.T.} = 8.37 + 0.000394\,T + 3.167 \times 10^{-7}\,T^2$.

Methane. Lewis and Randall give an approximate equation for the molecular heat of methane, which does not agree with the later results of Dixon, Campbell and Parker[3]. The curve C^p_T/T for methane shows a very rapid change in the molecular heat at ordinary temperatures. Thus, from 373°K to 273°K, the molecular heat falls from 10.6 to 8.6, while from 273°K to 173°K, the change is only from 8.6 to 7.9. Both Lewis and Dixon give linear equations which cannot possibly represent this very accurately.

Dixon gives $C_p^t = 8.66 + 0.019\,t$, which becomes

$C_p^T = 3.47 + 0.019\,T$.

Lewis and Randall give $C_p^T = 7.5 + 0.005\,T$.

Dixon's results are employed for the determination of the $\beta^1 + b^1$ term in the methane equilibrium.

Acetylene. Only a few values for the molecular heat of acetylene are available, which, unfortunately, are for temperatures below 273°K. These values show that its molecular heat is a little greater than that of methane. The same value as for methane is used.

Cyanogen. No values for the molecular heat of this gas have been determined. The same value as for acetylene is therefore used.

Ammonia. The values for the molecular heat of ammonia are not very concordant. At room temperatures, the agreement between values given by different workers is moderate, but at higher temperatures, considerable variations are present. The work of Haber[2] shows ammonia to have a greater molecular heat than that found by Nernst[3] for the temperature region 600-900°K. At high temperatures, the researches of Budde[1], who used the explosion method, are available, but, if extrapolated to 1000°K, they give values some 16 per cent lower than those given by Haber. The following equation is selected:—

$$C_p^{O.T.} = 7.60 + 0.0012\,T + 7.17\,10^{-7}\,T^2.$$

The values given by this equation are correct at room temperatures but somewhat lower than those given by Haber (for 600-900°K), and higher than those given by Budde (1400-2000°K). The equation given by Haber, which is applicable to 1000°K, is

$$C_p^{O.T.} = 8.04 + 0.00035\,T + 0.0000017\,T^2$$

Heats of Reaction

The heats of reaction at room temperature (taken as 293_2K) chosen for practical use, are the mean of the values given in Landolt and Börnstein's[4] "Tabellen", 1923.

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[1] l.c.

[2] Z. Elektrochem. 20, 597 (1914).

[3] Z. Elektrochem, 16, 96 (1910).

[4] Z. anorg. Chem. 78, 159 (1912).

The figures given below, represent the heat evolved in the reaction from left to right, at constant pressure (atmospheric) at 293°K, and are expressed in gram calories (the calorie at 15°C) all substances except carbon, being considered in the gaseous state.

For the reaction

$$2\ H_2+O_2=2\ H_2O,$$

the values in the literature are in good agreement with each other. As a mean, the value 115, 660 is used.

With regard to the reactions involving carbon, graphite is taken for the basis of calculation, and corrections have been made for the experimental determinations in which diamond and amorphous carbon are used.

The mean of the values of Thomsen, Berthelot and Roth, give for amorphous carbon

$$C_{am} + O_2 = CO_2 + 97,\ 170 \text{ cal..}$$

The mean of the values given by Berthelot and Roth for diamond and graphite, are

$C_{di.} + O_2 = CO_2 + 94,\ 370$ cal..

$C_{gr.} + o_2 = CO_2 + 94,\ 550$ cal..

From these,

$C_{gr.} = C_{di.} + 180$ cal., and

$C_{gr.} = C_{am} - 2{,}620$ cal..

These values are used to convert diamond and amorphous carbon to graphite. Taking the mean values, we get for graphite

$C + \frac{1}{2}O_2 = CO + 26,\ 330$ cal..

$C + O_2 = CO_2 + 94,\ 550$ cal..

From these, $2\ CO + O_2 = 2\ CO_2 + 136,\ 440$ cal.,

and $C + CO_2 = 2\ CO - 41,\ 890$ cal..

In cases in which the heat of formation is obtained from experimental determinations of the heat of combustion, as for example, in the case of HCN, C_2H_2, and CH_4, the value for the heat of formation as given by the experimenter is used, and this value corrected to the graphitic form of carbon if necessary. In this way, taking the mean of the values given by Thomsen and Berthelot, we get

$2\ C + H_2 + N_2 = 2\ HCN - 60,\ 420$ cal.,

$C + 2\ H_2 = CH_4 + 19,\ 100$ cal.,

$2\ C + N_2 = C_2N_2 - 72,\ 240$ cal..

The mean of the values of Thomsen, Berthelot and Mixter corrected to graphitic carbon give, for acetylene

$$2\ C + H_2 = C_2H_2 - 54{,}000 \text{ cal..}$$

Taking the mean of the values of Thomsen, Berthelot and Haber for the ammonia synthesis, we get

$$N_2 + 3\ H_2 = 2\ HN_3 + 23{,}390 \text{ cal..}$$

For nitric oxide, Thomsen and Berthelot give

$$N_2 + O_2 = 2\ NO - 43{,}200 \text{ cal..}$$

Chemical Constants

The best methods for the calculation of the chemical constant involve the assumption made in equation (16), that

$C_p^0 = \alpha = 3.5 + 1.5 \times n$ where n is the number of atoms in the molecule of the substance concerned. The difference between C_p^0 given by this equation, and α^1 is small, so that the error produced in the calculation of C, the chemical constant, is quite negligible. For this reason, the values for the "Conventional Chemical Constants" given by Nernst[1] are used. In cases where a value is not given, it is calculated:—

I. By the van der Waals—Nernst expression

$$\log\frac{\pi}{p} = a\left(\frac{\tau}{T} - 1\right) \;;\quad C = 1.1\ a\ .$$

where π and τ are the critical pressure and temperature, and T is the boiling point under pressure p.

II. By the Trouton—Nernst expression

$$C = 0.14 \cdot \frac{\lambda}{T}$$

Where λ is the molecular heat of vaporisation at the boiling point, T°K

In no cases where Nernst does not give a value are there sufficient data to substitute in his more accurate equation involving vapour pressure and critical data.

The values used are:—

H_2	N_2	H_2O	O_2	CO	CH_4
1.6	2.6	3.6	2.8	3.5	2.5
CO_2	NH_3	HCN	C_2H_2	C_2N_2	NO
3.2	3.4	3.8	3.2	3.4	3.2

Nernst gives the value 3.5 for NO.

Equations for the Equilibrium Constant Calculation

The value for the heat of reaction at 20°C is converted to the value Q'_0 using equation (12). This value of Q'_0 is then used, together with the α^1, a^1, etc. terms for the molecular heats, and the algebraic sum of the chemical constants, for the determination of ln Kp, equation (13) being employed unless otherwise stated. The results are compared with experimental results where these are available.

$$2\,H_2 + O_2 = 2\,H_2O$$

The experimental determination of this equilibrium has been carried out in several ways. Langmuir[2] heated a platinum wire in water vapour, Nernst and v. Wartenberg[3] used a dynamic method, and Löwenstein[4] used a semi-

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[1] "Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes," (1918).

[2] J. Am. Chem. Soc., **28**, 1357 (1906).

[3] Z. physik. Chem., **56**, 513 (1906).

[4] Z. physik. Chem., **54**, 715 (1905).

permeable platinum tube for the measurement of the partial pressure of the hydrogen. The experiments by Bjerrum[1], who used the explosion method, give values up to 3000°K, but are not as accurate as the determinations at lower temperatures.

The experimental values given in the following table were read off from a smooth graph of $\log K_p/T$ which passed through the various experimental values.

The equation derived from the data given is

$$\log K_p = \frac{25{,}050}{T} - 2.055 \log T - 0.0001\,345\,T + 6.923 \times 10^{-8}\,T^2 + 1.2$$

TABLE I $\qquad K_p = \frac{p^2_{H_2O}}{p^2_{H_2} \cdot p_{O_2}}$

T°K	log K_p calcd.	log K_p exptl.	Author.
1200	15.68	15.63	Nernst-v. Wartenberg and Langmuir.
1400	12.55	12.45	" " "
1600	10.24	10.29	" " "
1800	8.41	8.52	" " " and Löwenstein.
2000	6.95	7.02	" " " "
2200	5.75	5.78	Nernst and v. Wartenberg.
2400	4.76	4.80	" "
2600	3.93	4.00	Bjerrum.
2800	3.23	3.40	"
3000	2.63	3.0 about	"

$$2\,CO + O_2 = 2\,CO_2$$

The experimental study of this reaction is very similar to the previous one. Nernst and v. Wartenberg[2], Langmuir[3], and Bjerrum[4], used the same method as for the water equilibrium, but Löwenstein[5] used a modification of the Victor Meyer method.

The experimental results in Table 2, were obtained graphically as in the previous case.

$$K_p = \frac{p^2_{CO_2}}{p^2_{CO} \cdot p_{O_2}}$$

$$\log K_p = \frac{29{,}630}{T} - 2.275 \log T + 0.001143\,T - 1.335 \times 10^{-7}\,T^2 - 3.4$$

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[1] Z. physik. Chem., 79, 513 (1912).
[2] Z. physik. Chem., 56, 548 (1906).
[3] l.c.
[4] Z. physik. Chem., 79, 537 (1912).
[5] Z. physik. Chem., 54, 707 (1905).

TABLE II

T°K	log K_p calcd.	log K_p exptl.	Author.
1200	15.46	15.48	Nernst and v. Wartenberg.
1400	11.95	11.78	" " and Langmuir.
1600	9.30	9.40	" " "
1800	7.27	7.48	Löwenstein.
2000	5.65	5.8 about	Löwenstein Bjerrum.
2200	4.36	4.6 "	" "
2400	3.22	3.6 "	" "
2600	2.29	2.7	Bjerrum.
2800	1.48	1.9	"
3000	0.79	1.4	"

In reactions involving elementary carbon at 1000°K and over, we can assume that the surface of the carbon is graphitised, and that the equilibrium produced between this and the various gases, corresponds to graphitic carbon. The equations obtained from the data given, will therefore be applicable to these equilibria.

$$C + CO_2 = 2\ CO$$

The most reliable values for the equilibrium constant for this reaction are those by Rhead and Wheeler[1], who used the dynamic method. Those by Boudouard[2], and Arndt and Schraube[3], using the static method, and by Mayer and Jacoby[4] who used both methods, give lower values for the equilibrium constant than do Rhead and Wheeler.

In obtaining the curve $\log K_p/T$, from which the experimental values given in Table III were read off, the results of Boudouard, Arndt and Schraube, and Mayer and Jacoby were used up to 1100°K, (the lower temperature limit of Rhead and Wheeler), but beyond this, the Rhead and Wheeler values were used.

$$\log K_p = -\frac{8{,}975}{T} + 2.10 \log T - 0.000972\ T + 0.09 \times 10^{-8}\ T^2 + 3.8$$

$$K_p = \frac{p^2_{CO}}{p_{CO_2}}$$

TABLE III

T°K	log Kp calcd.	log Kp exptl.	Author
900	−0.77	−0.75	Boudouard, Arndt & Schraube.
1000	+0.23	+0.22	and Mayer & Jacoby.
1200	1.74	1.78	Rhead and Wheeler.
1400	2.80	2.90	" "
1600	3.58	3.65 about.	" "

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[1] J. Chem. Soc., 97, 2178 (1910).

[2] Ann. Chim. Phys., (7) 24, 5 (1901).

[3] Nernst-Festschrift, 46, (1912).

[4] J. Gasbeleuchtg., 52, 305 (1909).

$$2\ C + H_2 + N_2 = 2\ HCN$$

The only experiments available for this equilibrium are those of v. Wartenberg[1], who passed nitrogen and hydrogen mixtures over carbon in an electric furnace at 1908-2148°K. The equilibrium constant was estimated by extrapolation to zero velocity of gas flow, and is not very accurate.

v. Wartenberg estimated the value 4 for the chemical constant of hydrocyanic acid. The Trouton-Nernst approximate formula gives the value 2.7, which is certainly too low. As, however, from the similarity between hydrocyanic acid and water, the chemical constant is probably very near that of water, 3.6, the mean of this and the v. Wartenberg value is taken, i.e. CHCN = 3.8.

$$\log K_p = -\frac{13{,}210}{T} + 0.625 \log T - 0.0009\,515\,T + 1.18 \times 10^{-7} \times T^2 + 3\,4.$$

$$K_p = \frac{p_{H_2}}{p_{N_2}}$$

At T = 2000°K, v. Wartenberg found $\log K_p = -2.5$. The above equation gives the value -2.57

$$C + 2\ H_2 = CH_4$$

Mayer and Altmayer[2] investigated this reaction in the temperature region of 7 – 900°K. They used amorphous carbon containing a nickel catalyst, and because of the relatively low temperatures at which they worked, the equilibrium corresponded to amorphous carbon. In equation I, below, allowance has been made for this.

Pring and Fairlie[3] give the equilibrium constants for graphite at somewhat higher temperatures, their results being compared with equation II which refers to graphitic carbon.

With regard to the theoretical calculation of the equilibrium constants, we have seen that the molecular heat equation for methane is unknown, but by using the results of Dixon, Campbell and Parker[4], and extrapolating for about 100°, we find $C_p^{1000°}$K is 22.3. (1000°K is the mean of the temperature region investigated.) This value is then used in equation (17), page 1154, and the resultant value for the b^1 and β^1, and Q_o^1 terms substituted in equation (13), page 1153, the c^1 and γ^1 term being neglected.

The mean of Thomsen's and Berthelot's values for the heat of formation of methane from amorphous carbon is 21, 730 cal at 293°K.

For amorphous carbon,

$$\log K_p = \frac{4{,}583}{T} - 1.75 \log T + 0.000630\,T - 0.7 \quad \ldots\ldots\ldots\ldots (I)$$

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[1] Z. anorg. Chem. 52, 299 (1907).

[2] Ber. 40, 2134 (1907).

[3] J. Chem. Soc., 101, 91 (1912).

[4] Proc. Roy. Soc. 100 A, 1 (1921).

For graphite,

$$\log K_p = \frac{4{,}008}{T} - 1.75 \log T + 0.000630\, T - 0.7 \quad \ldots\ldots\ldots (II)$$

$$\log K_p = \frac{p_{CH_4}}{p^2_{H_2}}$$

TABLE IV

T°K	log K_p calcd.	Eqn..	log K_p exptl.	Author
600	2.45	(I)	2.5 about.	Mayer and Altmayer.
800	0.45	(I)	0.40	" "
900	−0.21	(I)	−0.37	" "
1000	−0.74	(I)	−1.0 about.	" " and Pring & Fairlie.
	−1.31	(II)		
1200	−1.99	(II)	−1.9 "	" "
1400	−2.45	(II)	−2.50	Pring and Fairlie.
1600	−2.79	(II)	−2.90	" "
1800	−3.04	(II)	−3.16	" "
2000	−3.22	(II)	−3.3 about.	" "

$$2\,C + H_2 = C_2H_2$$

The experimental determination of the equilibrium constant of this reaction has been carried out by v. Wartenberg[1] using the same method as for the hydrocyanic acid synthesis. The results are still less reliable in this case.

In the theoretical calculation of Kp the molecular heat of acetylene is assumed to be equal to that of methane, and the approximate equations (17), and (18), are used.

The van der Waals-Nernst equation for the determination of the chemical constant leads to the value 3.2 for acetylene, while the approximate Trouton-Nernst equation gives 3.7. The more accurate value 3.2 is used.

$$\log K_p = -\frac{11{,}770}{T} + 0.0004812\, T + 1.6.$$

$$\log K_p = \frac{p_{C_2H_2}}{p_{H_2}}$$

At $T = 2100°K$, v. Wartenberg found $\log K_p = -2.89$; the above equation gives the value -3.00.

$$2\,C + N_2 = C_2N_2$$

No experimental determination of the equilibrium constant of this reaction has yet been made.

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[1] Z. anorg. Chem., 52, 299 (1907).

The theoretical calculation is very similar to that for the acetylene synthesis. The van der Waals-Nernst equation leads to the value 3.4 for the chemical constant of cyanogen. This value is used.

$$\log K_p = -\frac{15{,}800}{T} + 0.0004704\,T + 0.8$$

$$K_p = \frac{p_{C_2N_2}}{p_{N_2}}$$

At 3500°K, which is approximately the temperature of the electric arc, $\log Kp = -2.07$, corresponding to the formation of 0.8 per cent cyanogen from nitrogen at atmospheric pressure. In actual practice, no trace of cyanogen is found, although spectroscopic observations show the presence of the cyanogen spectrum. Whether this spectrum is due to nitrogen or cyanogen is now a matter of controversy.

$$N_2 + 3\,H_2 = 2\,NH_3.$$

The investigaton of this important equilibrium has been carried out recently by Haber[1], and still more recently by Larson and Dodge[2]. Most of these experiments have been carried out under pressure, and although Larson[3] has shown that this causes a change in K_p, the effect is negligible at the lower pressures.

The use of equation (13), page 1153, which is employed for precious reactions leads to the equation $K_p =$

$$\log K_p = \frac{4790}{T} - 5.38 \log T + 0.0001225\,T + 1.569 \times 10^{-7}\,T_2 - 0.8$$

$$K_p = \frac{p^2_{NH_3}}{p^3_{H_2} \cdot p_{N_2}}$$

which gives values considerably different from experimental ones. Thus at 1000°K, the value of $\log K_p$ from this equation is -12, whereas the experimental value is -7.4. The cause of this discrepancy is unknown.

If, however, we employ equation (15), page 1154, we get

$$\log K_p = \frac{4686}{T} - 3.5 \log T + 0.0001225\,T + 1.569\,10^{-7}\,T^2 - 0.8$$

The results from this equation agree much better with the experimental values, the comparison being shown in Table V.

TABLE V

T°K	log K_p calcd.	log K_p exptl.	Author
600	−2.60	−2.8	Larson and Dodge.
800	−4.90	−5.0	Haber
1000	−6.33	−6.48	"
1200	−7.30	−7.43	"
1400	−7.97	−8.17	"

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[1] Z. f. Elektrochem. 20, 597 (1914).

[2] J. Am. Chem. Soc., 45, 2918 (1923).

[3] J. Am. Chem. Soc., 46, 367 (1924).

$$N_2 + O_2 = 2\,NO$$

Nernst[1] investigated this reaction by passing air through an electrically heated tube, the rate of passage of the gas being slow enough to ensure equilibrium.

If we use the Nernst value 3.5 for the chemical constant of nitric oxide, the theoretical calculation of logKp does not agree with the experimental values. 3.2 gives far better agreement, and is therefore used here.

$$\log K_p = -\frac{9452}{T} + 1.0.$$

$$K_p = \frac{p^2_{NO}}{p_{N_2} \cdot p_{O_2}}$$

TABLE VI

T°K.	log K_p calcd.	log K_p exptl.	Author.
1800	−4.25	−4.12	Nernst
2000	−3.73	−3.67	"
2200	−3.30	−3.21	"
2400	−2.94	−2.82	"
2600	−2.64	−2.53	"

$$H_2 + CO_2 = H_2O + CO$$

This reaction has been studied by a large number of workers with fairly concordant results. The work of Hahn[2], who approached equilibrium from both sides, by passing the gases over heated platinum as a catalyst, and Haber and Richardt[3] on flames, may be taken as representative.

The theoretical equilibrium constant for this reaction is obtained as follows

If K'_p is the equilibrium constant for

$$2H_2 + O_2 = 2\,H_2O,$$

$$\text{i.e.}\quad K^{I}_p = \frac{p^2_{H_2O}}{p^2_{H_2} \cdot p_{O_2}}$$

and K^{II}_p is the equilibrium constant for

$$2\,CO + O_2 = 2\,CO_2$$

$$\text{i.e.}\quad K^{II}_p = \frac{p^2_{CO_2}}{p^2_{CO} \cdot p_{O_2}}$$

Then the equilibrium constant for the reaction

$$H_2 + CO_2 = H_2O + CO$$

$$\text{is } K_p = \frac{p_{H_2O} \cdot p_{CO}}{p_{H_2} \cdot p_{CO_2}} = \sqrt{\frac{K^{I}_p}{K^{II}_p}}$$

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[1] Z. anorg. Chem., 49, 213 (1906).

[2] Z. physik. Chem., 44, 513 (1903); 48, 735 (1904).

[3] Z. anorg. Chem., 38, 5 (1904).

TABLE VII

T°K	K_p calcd.	K_p exptl.	Author.
800	0.20	0.2 about	Hahn.
1000	0.71	0.65	"
1200	1.29	1.32	"
1400	2.04	2.08	"
1600	2.95	2.95	Haber and Richardt.
1800	3.72	3.80	" "
2000	4.68	4.7 about	" "

Conclusion

Values for the mean molecular heats of gases at constant pressure, between 0°K and T°K, obtained from experimental values for the mean molecular heats between 273°K and T°K, by extrapolation to 0°K, have been used, together with the Nernst conventional chemical constants and the heat of reaction at room temperature, for the calculation of equilibrium constants. The assumptions made and the empirical nature of the equations obtained are fully realised. Except for the reaction resulting in the synthesis of ammonia, where the Nernst assumption with regard to the molecular heats was made, the equations obtained agree with experimental results.

The author wishes to express his best thanks to Mr. W. E. Garner who suggested this investigation, and for his valuable advice during the course of this work.

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THE BINARY SYSTEM SODIUM METASILICATE-SILICA

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This investigation of the melting point relations in the binary system sodium metasilicate-silica was undertaken primarily because of its importance as an end-member of more complicated systems of direct petrologic bearing; in particular, those formed by the addition of alumina and water, which are at present being studied by us. Publication of this material by itself was, however, deemed advisable because of the considerable technologic interest in this system, not only by reason of its bearing on the problem of the important soda-lime glasses, but also as constituting in itself a major chemical industry. The manufacture of silicate of soda has grown to be one of the largest chemical industries, and one whose ramifications rival those of sulfuric acid. The study of the ternary system formed by adding water to the sodium silicate-silica system is well under way, and a separate study of the mixtures richer in alkali than the metasilicate, both of sodium and of potassium, is planned.

Altho this system is of considerable technical importance, little has been published in regard to it. The two compounds which appear, sodium metasilicate, $Na_2O.SiO_2$ and sodium disilicate, $Na_2O.2SiO_2$, were prepared by Morey[1], and described by him. Niggli[2], in studying the reaction between Na_2CO_3 and SiO_2, also prepared sodium metasilicate, and includes some crystallographic and optical data by Fenner. Niggli also states that, "When sodium carbonate was heated with more than one equivalent of quartz, the product was, in my experiments, always sodium metasilicate mixed with quartz," but he also points out that his experiments give "no evidence against the formation under other conditions of an anhydrous sodium silicate containing more than one equivalent of silica," and mentions the preparation of sodium disilicate under hydrothermal conditions by Morey. Kultascheff[3] determined the melting point of sodium metasilicate and gives a value of 1007°. He did not analyze his material, tho he cites experiments which show that a melt of this composition at about its melting point loses 4.8 per cent Na_2O in an hour. His low result is accordingly to be ascribed to the presence of a considerable excess of SiO_2. Van Klooster[4] determined the melting point of sodium metasilicate, using a material prepared by ignition of Kahlbaum's crystalline hydrated sodium metasilicate. He also did not analyze his preparation, and his value, 1056°, is doubtless low. Several lots of Kahlbaum's crystalline sodium metasilicate analyzed by us showed the

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[1] J. Am. Chem. Soc., 36, 215-30 (1914).

[2] P. Niggli: J. Am. Chem. Soc., 35, 1693 (1913).

[3] N. V. Kultascheff: Z. anorg. Chem., 35, 186-93 (1903).

[4] H. S. van Klooster: Z. anorg. Chem., 69, 135-57 (1910).

presence of an excess of sodium oxide, and it is probable that his preparation was more soda-rich than the metasilicate. Wallace[1] studied this binary system, but did not succeed in determining any of the melting point curve, nor did he prepare the disilicate. He gives 1018° as the melting point of sodium metasilicate, but fails to give analyses of his material, and probably was not dealing with a mixture of exactly the composition of the metasilicate. In working with the alkali oxides at high temperatures, account must be taken of the volatilization of alkali, especially before decomposition of the carbonate or hydroxide is complete. Wallace also concluded that Na_2SiO_3 takes SiO_2 into solid solution, but his evidence is little more than conjectural. No evidence of solid solution was obtained in this study, either between sodium metasilicate and sodium disilicate, or between sodium disilicate and quartz, altho the method of study was particularly favorable to the detection of any such solid solution formation. Jaeger[2] made a determination of the melting point of sodium metasilicate on material carefully prepared and analyzed, and his value, 1088°, has been confirmed by us.

Preparation and Analysis of Materials

The raw materials used throughout were quartz and sodium carbonate. The former was a well washed sample, 10 g. of which showed a residue of 0.0077 g. after evaporation with HF and H_2SO_4 and subsequent heating with $(NH_4)_2CO_3$. The sodium carbonate contained but 0.9 mg. $Fe_2O_3+Al_2O_3$ in 10 grams. The materials were mixed in the desired proportions, and melted in platinum, either over a Meker burner or in a gas or electric furnace. The charges were usually calculated to give 10 or 25 grams of glass. After the glass appeared clear and free from bubbles it was quickly cooled, either by placing the crucible on an iron plate or by holding it in water, then the glass was broken out of the platinum crucible and pulverized. It was tested for homogeneity by examination with the petrographic microscope, using an immersion liquid matching it to within 0.005 in refractive index, and if not homogeneous again heated and powdered. The only glasses that required more than two heatings to become homogeneous were those containing 90 and 95 per cent SiO_2, which required three.

Glasses of exactly the composition of the disilicate were prepared by weighing the carefully analyzed quartz into a weighed platinum crucible, adding a slight excess of sodium carbonate, and melting to a clear glass, taking care to avoid loss from spattering. The cooled melt was then weighed, broken out of the crucible and pulverized. The powder, of known composition, was again weighed into a weighed crucible, a slight excess over the calculated amount of sodium carbonate necessary to bring the mass to the desired composition added, and the charge again melted to a clear glass. Heating was then continued until the charge had the desired composition, as determined by the weight after cooling, after which it was again broken

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[1] Z. anorg. Chem., 63, 1-48 (1909).

[2] J. Wash. Acad. Sci., 1, 49-53 (1911).

up and tested for homogeneity. If not homogeneous, the same procedure was followed until a homogeneous melt of the desired composition was obtained. The composition was always checked by analysis.

The resulting glasses differed widely in their tendency to crystallize. Sodium metasilicate and mixtures near it in composition crystallize readily. While no difficulty was experienced in obtaining glasses with the small charges used, it is doubtful if large meltings could be obtained. A glass of the composition of the metasilicate-disilicate eutectic is easily obtained; on the other hand, a few hours' heating at the appropriate temperature suffices to crystallize it almost completely. The compound sodium disilicate, which has not been prepared, hitherto, in the dry way, is easy to crystallize, a few hours' heating being sufficient to obtain a homogeneous melt to that composition in the crystalline condition. Mixtures slightly richer in silica than the disilicate-quartz eutectic are the most difficult to crystallize, but even they may be completely devitrified by heating below the eutectic temperature for a day or two. For example, a mixture containing 32 per cent Na_2SiO_3, 68 per cent SiO_2 was heated for 3 days at 750°, and the product was entirely crystallized as $Na_2O.2SiO_2$ and high-quartz. In spite of the high viscosity of the melt at this temperature, the quartz was in the form of well-terminated dihexahedrons characteristic of high-temperature quartz. This is the first time that quartz has been obtained in the dry way without the aid of fluxes. Some of these crystals were isolated by first digesting with water, then removing the coating of gelatinous silica by rapid treatment with dilute HF. It is noteworthy that prolonged digestion of this material on the steam bath with water alone or with sodium carbonate resulted in complete solution of the quartz. Methods for the separation of amorphous silica from quartz based on a difference in the rate of solution are evidently to be used with caution.[1] These mixtures were also crystallized by heating in bombs with water, as described in a previous publication[2]. Approximately 5 grams were placed in a gold crucible and heated with 5 cc. of water in a volume of about 80 cc. at 500° over night; the product was entirely crystalline. Mixtures in which tridymite and cristobalite are solid phases proved easier to crystallize, probably because of the lower viscosity at the higher temperature. Mixtures very rich in silica, such as that containing 95 per cent SiO_2, were difficult to obtain in the form of glasses, cristobalite separating out even when a 10 g. melt was plunged as quickly as possible into water. Glass of this composition was, however, obtained by quenching a few milligrams in mercury from a temperature above its liquidus. Incidentally, it should be noted that in one case a charge of this composition, which was removed from the furnace above the liquidus temperature and quenched by means of a blast of air, developed crystals of quartz.

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[1] Cf. Hillebrand: "The Analysis of Silicate and Carbonate Rocks." U. S. Geol. Survey Bull. 700, pp. 244-5.

[2] Morey: J. Am. Chem. Soc., 36, 215-30 (1914).

The analytical methods used were simple. It was shown by Niggli that even at 956° all the CO_2 is expelled from Na_2CO_3 by heating with one equivalent of SiO_2. With the higher temperatures used in preparing our melts, and their greater SiO_2 content, no difficulty was found in obtaining CO_2-free mixtures. As the ingredients were of high purity, and all the meltings were made in platinum, which does not contaminate the melt in mixtures containing so large a proportion of SiO_2, the glasses were truly binary mixtures, and hence determination of one constituent should suffice to fix the composition. Nevertheless, many glasses were analyzed by first digesting with water, to decompose them as completely as possible, then dehydrating the silica by two evaporations with strong HCl, with intervening filtration, as described by Hillebrand[1]. The precipitate was always checked by treatment with HF and H_2SO_4, and it was found that the amount of residue could be diminished by digesting the first silica with water, the filtrate being added to the first filtrate. The filtrate and washings from the second evaporation were collected in a 100 cc. gold crucible, in which the NaCl was weighed after evaporation and careful ignition. In the other glasses Na_2O was determined by weighing as Na_2SiF_6, as described in connection with the analysis of potassium silicates in a previous paper[2]. With sodium silicates it is advisable to decompose the more siliceous glasses by heating with water, before adding HF.

Experimental Methods

The melting point curve of the system Na_2SiO_3-SiO_2 was determined by the quenching method used so extensively in this Laboratory[3]. Small charges, a few milligrams, are wrapped in platinum foil, and held at a constant known temperature until equilibrium is reached. The charge is then quenched by dropping into mercury, usually by means of an electrical device or, in the case of glasses difficult to crystallize, by merely removing from the furnace and cooling in air. It was found that quenching was made more certain with substances which crystallize with extreme facility by fastening the charge to a small platinum weight, heavy enough to completely submerge the charge in the mercury. With some of the mixtures 15 minutes heating at constant temperature was sufficient to secure equilibrium, and identical results were obtained whether the mixture consisted initially of crystals or glass. With other mixtures, however, several hours were necessary, and in one case initial quartz persisted for several hours, 20° above the liquidus for that composition. In mixtures such as these the furnace regulator devised by Roberts[4] was an invaluable aid. With it temperatures could be maintained constant within half a degree for long periods. Mixtures close to the sodium disilicate-quartz eutectic were usually heated over night for the final runs. With one mixture (99.23 per cent Na_2SiO_3, 0.77 per cent SiO_2) a comparison was made between

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[1] Op. cit., p. 99.

[2] Morey and Fenner: J. Am. Chem. Soc., **39**, 1173-1229 (1917).

[3] Shepherd and Rankin: Am. J. Sci., **28**, 293 1909).

[4] H. S. Roberts: J. Wash. Acad. Sci., **11**, 401-409 (1921).

the melting point determined by quenching and determined by the usual time-temperature curve method, and the greater ease and certainty of interpretation with the quenching method[1] confirmed.

The thermoelement used was frequently calibrated, using as fixed points the melting points of NaCl and Na_2SO_4, determined by the heating curve method[2], and the melting points of Li_2SiO_3 and anorthite[3], determined by the quenching method. Quenching of the Li_2SiO_3 was greatly facilitated by the use of the platinum weight previously mentioned. The melting point of the 95 per cent SiO_2 mixture was determined by J. W. Greig, with a thermoelement calibrated by comparison with an element previously calibrated at the anorthite point and at the melting point of platinum.

TABLE I

Designation	Analysis Na_2O	SiO_2	Mol% Na_2SiO_3	Mol % SiO_2	Melting point	Solid phase
2154A	50.40	49.44	99.23	0.77	1086.5	Na_2SiO_3
2330A	45.88	54.03	82.32	17.68	1031.0	Na_2SiO_3
2142A	44.92	54.93	79.27	20.73	1001.	Na_2SiO_3
2115A	39.55	---	63.42	36.58	863.	Na_2SiO_3
2512A	37.83	---	60.85	39.15	847.	$Na_2Si_2O_5$
2144A	37.59	62.29	58.48	41.52	859.	$Na_2Si_2O_5$
2510A	35.90	---	54.29	45.71	871.	$Na_2Si_2O_5$
2518A	34.04	---	50.03	49.97	873.5	$Na_2Si_2O_5$
2414A	33.99	---	49.91	50.09	873.0	$Na_2Si_2O_5$
2034A	33.26	---	48.44	51.69	872.5	$Na_2Si_2O_5$
2411A	32.83	67.25	47.32	52.68	868.	$Na_2Si_2O_5$
2530A	29.20	---	39.97	60.03	831.	$Na_2Si_2O_5$
2530B	27.32	---	36.44	63.56	802.	$Na_2Si_2O_5$
2530C	25.78	---	33.27	66.73	830.	High quartz
2520A	24.81	---	31.99	68.01	841.	High quartz
2429A	19.54	---	23.55	76.45	1145.	Tridymite
2429B	11.67	---	12.51	87.49	1457.	Tridymite
2431A	4.07	---	5.12	94.88	1596.	Cristobalite

The results of this investigation are presented in Tables I and II, and in Fig. 1. Table I gives for each mixture the reference number, the weight per cent Na_2O or of both Na_2O and SiO_2, as determined, the calculated weight percentage of Na_2SiO_3 and SiO_2, the composition of the primary solid phase, and the liquidus temperature. In Table II are given for each mixture the essential experimental data upon which the thermal data of Table I are based, including for each run the temperature, the duration of the heating at that

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[1] Morey: J. Wash. Acad. Sci., 13, 326-9 (1923).

[2] Roberts: Phys. Rev., 23, 386-95 (1924).

[3] Day and Sosman: "High-temperature gas thermometry." Carnegie Inst. Washington, Publ. 157.

TABLE II

Glass	Temperature	Time	Condition
2154A	1085.6	15 min	crystals Na_2SiO_3
	1086.4	"	" "
	1086.5	"	glass and "
	1086.7	"	glass only
	1086.5		*Liquidus*
2330A	1025.7	15 min	glass and Na_2SiO_3
	1029.1	"	glass and rare Na_2SiO_3
	1032.6	"	glass only
	1031.		*Liquidus*
2142A	998.5	20 min	glass and Na_2SiO_3
	1000.2	"	glass and rare Na_2SiO_3
	1001.9	"	all glass
	1001.		*Liquidus*
2115A	858.4	20 min	glass and Na_2SiO_3
	860.2	"	" " little Na_2SiO_3
	864.7	"	all glass
	863.		*Liquidus*
2512A	840.2	20 min	Na_2SiO_3 and $Na_2Si_2O_5$
	844.7	"	glass and few $Na_2Si_2O_5$
	846.5	"	" " rare "
	848.4	"	all glass
	847.		*Liquidus*
2144A	840.2	20 min	Na_2SiO_3 and $Na_2Si_2O_5$
	849.3	"	glass and $Na_2Si_2O_5$
	858.4	"	" " "
	860.2	"	all glass
	859.		*Liquidus*
2510A	868.3	20 min	glass and $Na_2Si_2O_5$
	870.1	"	glass and rare $Na_2Si_2O_5$
	871.9	"	all glass
	871.		*Liquidus*
2518A	872.8	20 min	little glass and $Na_2Si_2O_5$
	873.3	"	glass and rare "
	873.7	"	all glass
	873.5		*Liquidus*
2414A	871.9	20 min	little glass and $Na_2Si_2O_5$
	872.8	"	glass* " "
	873.3	"	all glass
	873.0	"	*Liquidus*

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*Much more glass than in 2518A at this temperature.

TABLE II—(Continued).

Glass	Temperature	Time	Condition
2034A	870.6	20 min	glass and $Na_2Si_2O_5$
	871.5	"	" " little $Na_2Si_2O_5$
	873.3	"	all glass
	872.5		*Liquidus*
2411A	867.4	20 min	glass and rare $Na_2Si_2O_5$
	868.3	"	all glass
	868.		*Liquidus*
2530A	828.3	40 min	glass and $Na_2Si_2O_5$
	830.2	60 "	" " rare "
	832.0	"	all glass
	831.		*Liquidus*
2530B	786.2	90 min	glass and $Na_2Si_2O_5$
	797.2	"	" " little $Na_2Si_2O_5$
	800.0	"	" " few "
	803.6	"	all glass
	802.		*Liquidus*
2530C	827.4	4 hr	glass and quartz
	829.2	12 "	" " "
	830.2	4 "	all glass
	830.		*Liquidus*
2520A	838.	14 hr	glass and quartz
	845.	"	all glass
	841.		*Liquidus*
2429A	1140.7	1 hr	glass and tridymite
	1143.2	"	" " rare tridymite
	1147.4	"	all glass
	1145.		*Liquidus*
2429B	1446.6	1 hr	glass and tridymite
	1456.4	"	" " rare tridymite
	1459.0	30 min	all glass
	1457.		*Liquidus*
2431A	1583.	45 min	glass and cristobalite
	1592.	"	" " very little cristobalite
	1594.	"	" " rare cristobalite
	1596.		*Liquidus*

temperature, and the condition of the product. In a large proportion of the cases each experiment represents the result of heating side by side two charges, one initially crystalline, the other initially glass, and the results were always in accord. In the only cases in which both were not heated together, namely, some of the glasses rich in Na_2SiO_3, there was no question of the speedy attainment of equilibrium. Special attention should be called to the experiments with glasses 2510A, 2518A, 2034A, and 2414A, which are all close to the disilicate in composition. These were all put into the furnace and quenched together, and the thermoelement calibration checked immediately thereafter. The relative melting points of these mixtures are correct within 0.2°, and the actual temperatures within practically the same limits.

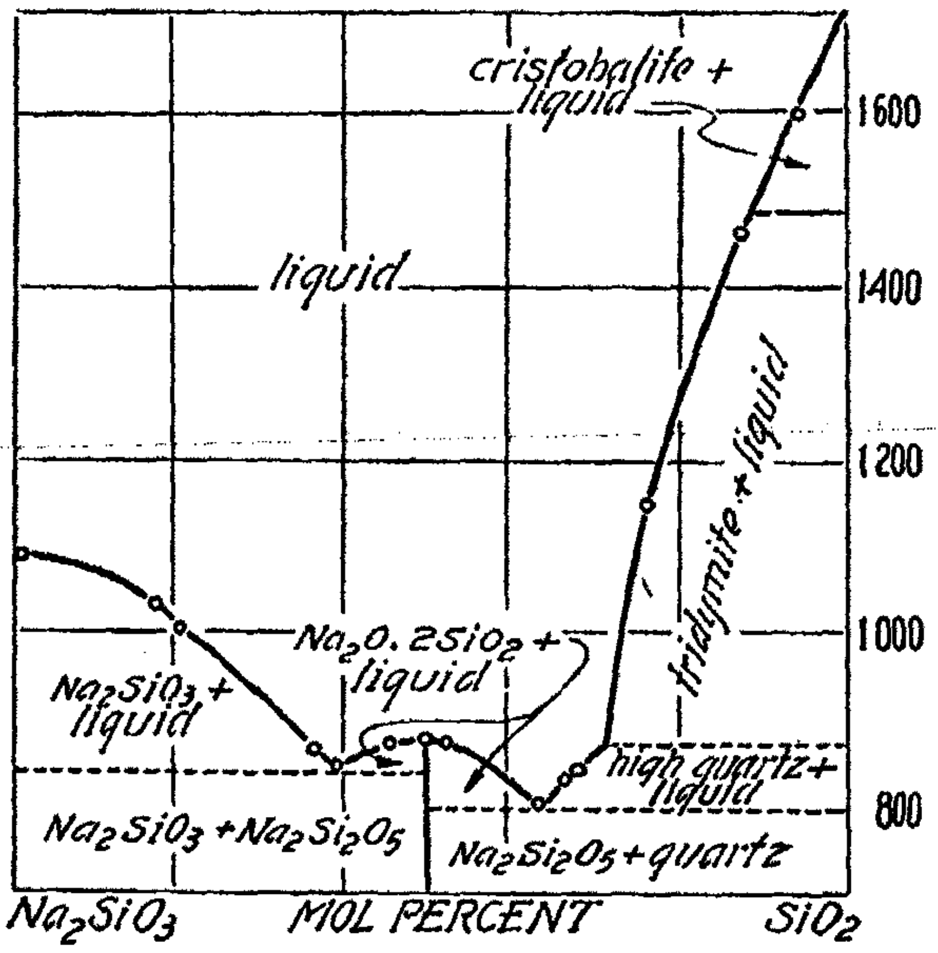

FIG. 1

Temperature composition diagram of the binary system Na_2SiO_3-SiO_2

Optical Properties of the Crystalline Phases

The two crystalline compounds sodium metasilicate and sodium disilicate do not differ very greatly in optical properties. Both have positive elongation and low refractive indices and are apparently orthorhombic in crystallization. They are to be distinguished only by precise measurement of their optical constants, which are given below in Table III.

Discussion of Results

The mixture nearest in composition to the metasilicate contains 0.77 mol percent excess silica, and its melting point was found to be 1086°. This was considered to be a sufficient confirmation of Jaeger's value of 1088° as the melting point of Na_2SiO_3, so there was no necessity of making up the pure

TABLE III

Optical Constants of Sodium Metasilicate and Sodium Disilicate

		Na_2SiO_3	$Na_2Si_2O_5$
Crystallization		orthorhombic	orthorhombic
Habit		needles	plates and needles
Cleavage		prismatic in zone of γ	pinacoidal $\parallel \gamma\beta$ and $\gamma\alpha$
Optic axial angle		2V very large	2V = 50 to 55°
Optical character		negative	negative
Refractive indices	γ	1.528 ± .002	1.518 ± .002
	β	1.520 ± .002	1.514 ± .002
	α	1.513 ± .002	1.504 ± .002

compound. Na_2SiO_3 remained the primary phase until the mixture containing 39.15 percent SiO_2 was reached, when the disilicate, $Na_2O.2SiO_2$, appeared as the primary phase. The eutectic was located by extrapolation of the metasilicate and disilicate curves, the temperature of the eutectic thus determined being 840°, the composition, 37.5 mol percent SiO_2. The shape of the two curves is such that but little uncertainty is introduced by this extrapolation.

Sodium disilicate, $Na_2O.2SiO_2$, has a congruent melting point at 874°. The melting-point curve is unusually flat, especially on the side toward Na_2SiO_3, the presence of 4.3 percent excess of the latter lowering the melting point only 2.5°. Addition of excess SiO_2 results in a more rapid lowering of the melting point, until the disilicate-quartz eutectic is reached. In this case the curves are both steep, and do not lend themselves so readily to determination of the eutectic temperature by extrapolation. The mixture with 63.56 percent SiO_2 melts at 802.7°, and the primary phase is $Na_2O.2SiO_2$; the mixture containing 66.73 percent SiO_2 melts at 827°, and high-quartz is the primary phase. The temperature of the eutectic was determined by holding these two preparations at successively increasing temperatures until the first sign of glass formation was observed, and both preparations gave the temperature as $793° \pm 1°$. With the eutectic temperature known, extrapolation of the two melting point curves becomes a more reliable method of locating the eutectic composition, which is estimated as 35 mol percent Na_2SiO_3, 65 percent SiO_2, or 26.5 percent Na_2O, 73.5 percent SiO_2.

Addition of Na_2O to silica produces a rapid lowering of the melting point, and there is no limited miscibility, such as has been found by Greig[1] in the systems formed by SiO_2 with CaO, MgO, and SrO. Addition of 4.07 percent Na_2O, giving a mixture containing 5.12 percent Na_2SiO_3 and 94.88 percent SiO_2, lowers the melting point from 1710°, the melting point of cristobalite,

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[1] A complete account of this work will appear in a forthcoming paper by Greig. A preliminary discussion was presented at the Christmas, 1923, meeting of the Geological Society of America.

to 1598°, with cristobalite as solid phase. Two points were determined on the very steep curve representing equilibrium between tridymite and liquid mixtures of increasing Na_2SiO_3 content, but these present no special features. The mixture containing 68 mol percent SiO_2 was crystallized by heating for three days at 750°. The crystals developed were high temperature quartz; on determining the melting point of this mixture by the quenching method quartz persisted until 842°, the liquidus for this mixture. This point was the most difficult of all to determine; in each run both crystals and glass were heated together at constant temperature for 14 hours, a shorter time not being sufficient either to dissolve the quartz above the liquidus or to form crystals in the glass below the liquidus.

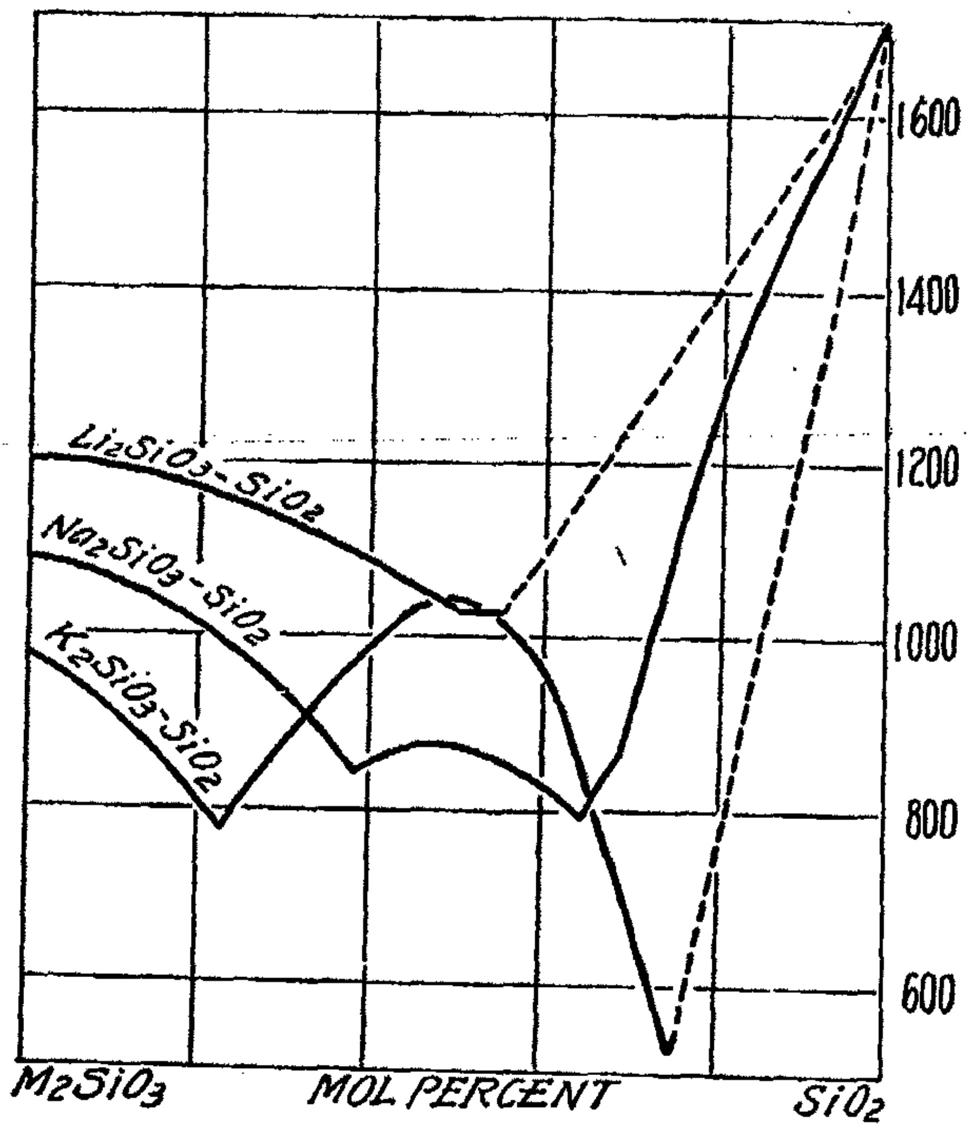

FIG. 2

Temperature composition diagram of the binary systems Li_2SiO_3-SiO_2, Na_2SiO_3-SiO_2, and K_2SiO_3-SiO_2.

Comparison of the Systems formed by SiO_2 with the Metasilicates of Lithium, Sodium, and Potassium

A comparison of the systems formed with silica by the other alkali metasilicates is of interest. The system Li_2SiO_3-SiO_2 was worked out by Jaeger and van Klooster[1], in a study which included also the mixtures approaching the orthosilicate in composition. The portion of their diagram from the metasilicate to SiO_2 is reproduced in Fig. 2. The system K_2SiO_3-SiO_2 was

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[1] Jaeger and van Klooster: Proc. Acad. Sci. Amsterdam, 16, 857-880 (1914).

treated incidentally by Morey and Fenner[2] in their study of the ternary system H_2O-K_2SiO_3-SiO_2, but the melting points of the anhydrous compounds K_2SiO_3 and $K_2O.2SiO_2$ were determined, as well as the isobaric polythermal saturation curves at one atmosphere pressure of water vapor.

The metasilicates of the three alkali metals show a uniform diminution of melting point with increasing atomic weight, Li_2SiO_3 melting at 1201°, Na_2SiO_3 at 1088°, and K_2SiO_3 at 976°. There is no such regularity in the melting points of the disilicate compounds, potassium disilicate melting at 1041°, sodium disilicate at 875°, while lithium disilicate has an incongruent melting point at 1032°. But when we consider the shape of the disilicate liquidus in each case, there is again a striking periodicity. The liquidus for $K_2O.2SiO_2$ rises to a well-defined maximum; the metasilicate-disilicate and the disilicate-quartz eutectic in the case of potassium are both at lower temperatures than the corresponding sodium eutectics, tho the potassium disilicate melts 157° higher. The sodium disilicate liquidus is unusually flat, there being a difference of only 35° between the temperature of the metasilicate-disilicate eutectic and the melting point of $Na_2O.2SiO_2$. Lithium disilicate shows a still flatter liquidus; the disilicate-tridymite eutectic is at 1029°. and the temperature of decomposition of the disilicate into metasilicate and liquid is 1032°, only 3° higher. This increasingly large amount of flattening of the melting point curve of the disilicate is to be ascribed to an increasingly large amount of dissociation in the liquid phase.

The theorem that the melting point or solubility curve has a maximum temperature, at constant pressure, at the point where liquid and solid phases have the same composition is usually ascribed to Lorenz and Stortenbeker[2], who derived the theorem, making use of Gibbs' zeta-function, apparently unaware that Gibbs himself had discussed this question in several places. In one place he[3] states, with reference to a two-component system: ". . . . two coexistent phases are capable, when the temperature is constant, of a single variation in phase. But as (130) will hold true in this case when $m_1' : m_2' :: m_1'' : m_2''$, it follows that for constant temperature the pressure is in general a maximum or a minimum when the composition of the two phases is identical. In like manner, the temperature of the two coexisting phases is in general a maximum or a minimum, for constant pressure, when the composition of the two phases is identical. . . . This may be applied to a liquid having two independently variable components in connection with the vapor which it yields, or in connection with any solid which may be formed from it." The subject is also discussed from the graphical point of view on page 119, in a section of his paper in which Gibbs lays the foundation of the present graphical method of treating problems of phase equilibrium. In a later section, during the course of a discussion "On the Value of the Poten-

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[2] Morey and Fenner: J. Am. Chem. Soc., 39, 1173-1229 (1917).

[2] Z. physik. Chem., 10, 183-202 (1892).

[3] "The Scientific Papers of J. Willard Gibbs," Vol. 1, page 99. Longmans, Green and Co.

tials when the Quantity of one of the Components is very small" (page 135), Gibbs discusses this case more extensively, and lays special stress on the distinction between the adding of a new substance to the mass in question, in which case the potential is lowered, and the adding of a substance which is present as one of the components of the mass, in which the potential is not altered.

The increased flattening of the disilicate curves in the series K-Na-Li is accordingly to be ascribed to an increased dissociation of the disilicate in the liquid phase; a dissociation not large in the case of potassium, but which is of considerable magnitude in the case of sodium, and which has become so great in the case of lithium that the compound can only exist in contact with liquids containing an excess of SiO_2. In the case of the reaction presumably existing in the liquid phase,

$$K_2Si_2O_5 = K_2SiO_3 + SiO_2,$$

the equilibrium at the melting point lies so far to the left that addition of either K_2SiO_3 or SiO_2 produces a marked effect in lowering the melting point. In the reaction

$$Na_2Si_2O_5 = Na_2SiO_3 + SiO_2,$$

the equilibrium has shifted so far to the right that addition of either product of dissociation does not greatly alter the proportion of molecular species present, and hence does not greatly affect the melting point. In the case of the reaction

$$Li_2Si_2O_5 = Li_2SiO_3 + SiO_2,$$

this process has taken place to a still greater extent. We thus have in the dissociation of the disilicates of these alkali metals a progressive increase in dissociation at the melting temperature with decreasing atomic weight. The correlation between the melting phenomena of the meta- and disilicates of the alkali metals with the present theories of atomic and molecular structure affords an interesting field for speculation.

Petrologic and Technologic Applications

The low temperature of the disilicate-quartz eutectics in both the potassium and sodium systems is a striking fact; one which is of fundamental importance both in petrology and in glass technology. In both cases the lowest temperatures in the systems are found in mixtures high in silica, and in both cases the melting temperatures are lower than ever before observed in anhydrous silicate systems. But it is not until we consider the addition of other components that the importance of these low-melting mixtures becomes evident. Addition of alumina to them will, of course, result in a further lowering of the melting point, until the ternary eutectics, at which quartz, feldspar and disilicate coexist in contact with liquid, are reached. The influence of these extremely low eutectics in the still more complicated magmatic systems is probably one of the factors which cause the feldspars and quartz to be the last phases to appear in the differentiation of the igneous rocks, and it may be of still more direct influence on the probably even more complex phenomena associated with the formation of pegmatites. The importance of this low temperature eutectic to glass technology is even more fundamental. The composition of the potassium disilicate eutectic is about 28 per cent K_2O, 72 percent SiO_2; that of the sodium disilicate eutectic, 26 percent Na_2O, 74 percent SiO_2. It is evident that addition of CaO to the eutectic mixture will lower the melting point, the lowest melting mixture being that of whatever ternary eutectic there may be in the system. But on addition of lime we pass at once into the field of the soda-lime-silica glasses, the type of glass which, as blown window glass and as plate glass, make up by far the major portion of the glass of commerce. The so-called "normal glass," as represented by the Benrath formula, $M_2O.CaO.6SiO_2$, may be taken as indicative of the usual types of these simple but industrially important glasses; for a soda glass this gives a composition 11.6 percent CaO, 13.2 percent Na_2O, and 75.2 percent SiO_2, and for a potash glass, 11 percent CaO, 18.4 percent K_2O and 70.6 percent SiO_2. It will be noticed that in each case these are approximately the compositions that would result from replacing a portion of the alkali at the disilicate-quartz eutectic by lime, a procedure that would result in a lowering of the eutectic temperature, until the region of the ternary eutectic had been passed. This ternary eutectic, moreover, is not the lowest melting mixture to be considered, as many glasses are of mixed composition, containing both potash and soda, and appreciable amounts of Fe_2O_3 and Al_2O_3 are usually present, each of which additional components will probably further lower the eutectic temperature. It appears probable, then, that most commercial glasses owe their power of resisting devitrification in their working range to the fact that in this range they are at a temperature higher than that at which crystallization should begin. In other words, they remain in the "glassy," that is, liquid condition because they are above the temperature at which crystallization could begin in a mixture of the given composition. A study of the melting phenomena in the ternary systems Na_2SiO_3-$CaSiO_3$-SiO_2 and K_2SiO_3-$CaSiO_3$-SiO_2 is at present under way, which it is hoped will clear up these interesting relationships.

Summary

The system Na_2SiO_3-SiO_2 is of a simple type, with one compound, sodium disilicate, $Na_2O.2SiO_2$, and no solid solutions. The melting point of Na_2SiO_3 is 1088° and the eutectic Na_2SiO_3-$Na_2O.2SiO_2$ is at 840°, 62.5 mol percent Na_2SiO_3, 37.5 mol percent SiO_2. $Na_2O.2SiO_2$ has a congruent melting point at 874°, and its melting point curve is characterized by an unusually flat maximum. The $Na_2O.2SiO_2$-quartz eutectic is at 793°, 35 mol percent Na_2SiO_3, 65 mol percent SiO_2. The significance of this low-melting eutectic in petrology and glass technology is discussed.

Geophysical Laboratory,
Carnegie Institution of Washington,
July, 1924.

THE FRACTIONATION OF BIOS, AND COMPARISON OF BIOS WITH VITAMINS B AND C

BY GEORGE H. W. LUCAS

The work described in the following pages grew out of the physico-chemical study of staphylococcus, anthrax and saccharomyces which has been carried on in this laboratory under direction of Prof. W. Lash Miller for a number of years. The first result of this study was that the toxicity of phenol solutions[1] towards these organisms depends primarily on the chemical potential of the phenol[2] in the solutions employed; the effect of the addition of a salt to the solution[3] can in most cases be quantitatively accounted for by the effect of the addition on the potential of the phenol contained in the solution. This cause of death, however, can be masked by the toxic effect of solutions whose osmotic pressures are low[4] and the effect of adaptability of the organism made itself felt as a disturbing element in the experimental work.

To gain more information on the latter point, a quantitative study of the acclimatization of yeast[5] to ammonium fluoride and its reversion was carried out. In these experiments ammonium fluoride was dissolved in wort; and, as unpublished work by Miss A. Roberts shewed that the results were much affected by modifying the medium, attempts were made to grow yeast in the various solutions of sugar and salts described in the literature. None of these proved comparable to wort as a culture medium for yeast; an explanation was found in the work of Wildiers[6] of Louvain whose experiments established the existence of an unknown substance, by him called Bios, which if not "*indispensable*[7] *au développement de la levûre*" at all events has an extraordinary effect in accelerating its reproduction. Since Wildiers' time, this substance has been studied by a number of authors some of whom rediscovered it for themselves.[8]

The study of this substance here was undertaken by Mr. N. A. Clark and myself. Mr. Clark's experiments shewed that, within wide limits, addition of wort to the salts and sugar solution leaves the rate of reproduction

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[1] W. Lash Miller: J. Phys. Chem. 24, 564 (1920); J. S. Lemon: 24, 570 (1920); J. S. Laird: 24, 664 (1920); C. G. Fraser: 24, 741 (1920), 25, 1 (1921); E. I. Fulmer: 25, 10 (1921).

[2] The maximum of toxicity exhibited by mercuric chloride when dissolved in 25% alcohol can be accounted for similarly. J. S. Laird: J. Phys. Chem. 24, 736 (1920).

[3] Discovered by Scheurlen: Arch. exp. Path. Pharm. 37, 74 (1895), and studied by Beckmann: Centralbl. Bakteriologie 20, Abt. 1, 577 (1896) and by Paul and Krönig: Z. Physik. Chem. 21, 414 (1896).

[4] J. S. Laird: J. Phys. Chem. 24, 664 (1920); K. E. Burgess: 24, 738 (1920).

[5] E. I. Fulmer: J. Phys. Chem. 26, 455 (1922).

[6] Wildiers: "La Cellule" 18, 313 (1901).

[7] Wildiers: *loc. cit.* For discussion of this point see Pringsheim: Cent. Bakt. Parasit. 16, 111 (1905); Ide: 18, 193 (1907), J. Biol. Chem. 46, 521 (1921); MacDonald and McCollum: J. Biol. Chem. 46, 525 (1921); Fulmer, Nelson and White: J. Biol. Chem. 57, 397 (1923); Funk and Friedman: Proc. Soc. exp. Biol. and Med. 20, 311 (1923).

[8] Amand: "La Cellule" 20, 223 (1903); 21, 327 (1904); Devloo: 23, 361 (1906); Ide: Cent. Bakt. Parasit. 18, 193 (1907); Bottomley: Proc. Roy. Soc. 88, B 237 (1914) were among the earliest.

unaffected, but regulates the yield or total crop;[1] he also studied the effect of alcohol, acetone and a number of other reagents[2] on the rate of reproduction of yeast, and laid the foundation for a convenient quantitative method for the determination of Bios[3]. My own experiments were directed to the isolation, or at least the concentration, of the active substance.

In the winter of 1919-1920 Mr. Clark found that when wort is decolorized by charcoal its efficiency as a reproduction-promoting factor is removed. I spent a lot of time endeavouring to recover the active substance from the charcoal; but, as is now apparent, these experiments were bound to be unsuccessful, since the charcoal takes up only one of the two constituents of which I subsequently found the Bios to be composed. The fractionation was accomplished in December 1921 and a short note of the results obtained and the method employed was published in May 1923[4] and a somewhat fuller account in January 1924[5]. The present paper contains the results of my experiments; those of Mr. H. des B. Sims on the purification of Bios I, of Mr. E. M. Sparling on the behaviour of Bios II with charcoal, and of Miss E. V. Eastcott on the mother-substances of Bios I and Bios II will shortly appear.

In April 1923 I carried out a number of experiments on the effect of Bios I and Bios II, and of mixtures of these, on polyneuritic pigeons in the laboratory of Prof. Clara C. Benson; and in May of the same year experiments with rats and guinea pigs were undertaken by Miss J. Deas in the laboratory of Prof. V. E. Henderson using material supplied by myself. The results show conclusively that my preparations are quite distinct from vitamins B and C. Last winter I subjected infusions of rice polishings (which contained vitamin B) to the chemical treatment which results in the fractionation of the Bios, and although two solutions were obtained containing Bios I and Bios II respectively, Miss Deas' experiments show that neither of them nor the two together has the physiological effect of vitamin B on rats. The treatment that results in fractionating Bios thus destroys the vitamin.

On the occasion of the recent visit of the British Association to Toronto, Prof. W. H. Eddy supplied us with a beautifully crystallized sample of the Bios prepared by him from yeast. Working by our method we were unable to obtain the yeast crop that Prof. Eddy had shortly before secured from the same preparation, and at our suggestion he was good enough to bring with him two cultures of the yeast used in his laboratory. One of these cultures behaved very like the yeast used here, both with Prof. Eddy's crystals and with our two Bios preparations; in a solution of salts and sugar alone its

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[1] N. A. Clark: J. Phys. Chem. **26**, 42 (1922).

[2] N. A. Clark: J. Phys. Chem. **28**, 221 (1924).

[3] Wildiers, Amand and Devloo measured the gas evolved by the yeast crop, so did Miss Bachmann: J. Biol. Chem. **39**, 235 (1919), and Heaton: Biochem. J. **16**, 800 (1922). Williams grew single yeast cells in a hanging drop: J. Biol. Chem. **42**, 259 (1920), **46**, 113 (1921); his method was adopted or modified by Emmett and Stockholm: J. Biol. Chem. **43**, 287 (1920), Eddy and Stevenson: **43**, 295 (1920), Swoboda: **44**, 551 (1920), Whipple: **44**, 175 (1920), Miller: **44**, 159 (1920).

[4] G. H. W. Lucas: Trans. Roy. Soc. Canada, Sec. III, page 157 (1923).

[5] W. Lash Miller: Science **59**, 197 (1924).

reproduction is very slight. The other culture, however, gave a high crop without addition of any Bios at all, although much more was obtained when Bios II or Bios I and II was present. This observation shews how necessary it is in work of this kind to control the strain of yeast employed, and no doubt explains repeated failures in this laboratory to duplicate the results obtained by Mr. Fulmer[1] with his medium E.

I. Apparatus and Methods Employed

The yeast used for seeding was obtained from a Fleischmann's yeast cake by plating on wort agar; the second plating was effected from a three-pronged colony on this first plate, and the third plating from a three-pronged colony on the second. Working in this manner we have never obtained a yeast culture that increased more than ten-fold when rocked 24 hours at 25°C in the artificial medium made with unpurified commercial cane sugar as described below. The yeast from the third plate was used to seed wort (prepared as described by Mr. Clark[2]) to a count of 1.0 or 2.0 which was left in an Erlenmeyer flask in a Freas' oven at 25°C, and used to seed the experimental tubes about 20 hours (but never more than 24 hours) after the flask had been seeded[3]. A new flask of wort was seeded each day from the culture of the day before; with care the culture could be kept going four months without contamination.

Determination of Bios: When the rocker tubes were ready for seeding, about 10 cc. of the well-shaken flask culture was filtered with suction on a small filter paper sterilized by alcohol; the yeast was washed about ten times with sterile water, and was suspended in sterile water to a count of 10; 1.0 cc. of this suspension was added to the contents of the tube viz. 5.0 cc. of the stock salts-and-sugar solution, a measured volume of the solution in which the Bios was to be determined, and enough water to bring the total contents of the rocker tube to 10.0 cc. after the yeast suspension had been added. The tube was then rocked in a thermostat at 25°C for 24 hours, after which the yeast crop was determined.

The rocker tubes were the L-shaped tubes described by Fraser[4] but smaller, total length being about 27 cm. with a bend in the middle; the capacity of the closed end to the bend was about 15 cc. The open ends were closed with cotton wool; twenty-four of these tubes could be slipped in a rack and rocked in a thermostat at 25°C. In the first experiments the contents of the tubes were sterilized by heating for half an hour in the steam sterilizer before adding the yeast suspension; it was found however, that by measuring sterilized salts and sugar solution and Bios extracts into sterile tubes with sterile pipettes, this additional sterilization could be avoided.

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[1] Fulmer, Nelson and Sherwood: J. Am. Chem. Soc. **43**, 191 (1921).

[2] N. A. Clark: J. Phys. Chem. **26**, 42 (1922).

[3] E. I. Fulmer: J. Phys. Chem. **25**, 10 (1921).

[4] C. G. Fraser: J. Phys. Chem. **25**, 4 (1921).

Determination of yeast crop: At first this was accomplished by means of the haemocytometer[1] hence the unit in which our yeast concentrations are recorded: one cell over each large square of the Thoma ruling corresponds to 250,000 cells per cc.; a "count" of 350, for instance, thus corresponds to 350×250,000 cells per cc. or 10×350×250,000 cells in the 10 cc. of liquid in the rocker tube. Afterwards the centrifugal method[2] was used: 2.0 cc. of the contents of the rocker tube was pipetted into a cylindrical tube of about 10 cc. capacity to the bottom of which a capillary extension was fused; some solution was then added which had the effect of hindering fermentation; the mixture was let stand five minutes, it was then centrifuged for 7 minutes, and the height of the column of yeast in the capillary determined by a millimetre scale, and converted into "count" by means of a previous calibration of the capillary with the haemocytometer (one millimetre corresponded to a count of about 10). One cc. of a solution containing 10 g of sodium chloride and 1.0 cc. of liquid phenol made up to 100 cc. stops fermentation without shrinking the cells; this works well under normal conditions and gives more constant results than the sodium hydrate used by Carlson; but for some purposes 2.0 cc. of normal chloracetic acid (introduced by Miss E. M. Taylor) is more satisfactory.

The artificial medium employed is that of Mr. N. A. Clark; its composition is much like that of Nägeli's solution but cane sugar is used in place of dextrose[3]. Purification of the cane sugar by charcoal[4] materially improves this medium from our point of view, for with a seeding of a "count" of 1 it cuts down the 24 hour crop of yeast from a count of 10 to a count of 5.

Determination of solids: For this purpose a measured volume of the liquid (usually 10 to 25 cc.) was left 24 hours or so in an oven at 105°C and the residue weighed.

Malt combings infusion ("root-brew"): In my first experiments wort was used as raw material; this substance however contains a large percentage of sugar which is difficult to remove and was abandoned in favor of an infusion of malt combings, i.e. of the dried rootlets of the sprouted barley, which was prepared as follows: 975 cc. of tap water is brought to boiling and 150 g of combings added with stirring, while the temperature is held between 80°C and 85°C for 10 to 15 minutes, during which time the roots become greatly swollen. The whole is then transferred to a press and squeezed as dry as possible. The yield of infusion varies from 650 cc. to 700 cc; it is light brown in colour and colloidal in appearance; its specific gravity varies from 1.016 to 1.024; 100 cc. dried for 24 hours at 105°C to 110°C leaves about 5 g

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[1] Used by Souza and McCollum: J. Biol. Chem. **44**, 113 (1920); Wright: Biochem. J. **16**, 137 (1922).

[2] Introduced by Carlson: Biochem. Z. **57**, 313 (1913); used by Funk and Dubin: J. Biol. Chem. **44**, 487 (1920), who heated the cells to 70°C to stop fermentation.

[3] The solution in the rocker tube contained per 100 cc: 0.417 g KH_2PO_4, 0.834 g NH_4NO_3, 0.071 g $CaCl_2 6H_2O$, 0.208 g $MgSO_4 7H_2O$, 10 g. cane sugar. For convenience the stock solution was made up to twice this strength.

[4] Funk and Friedman: Proc. Soc. exp. Biol. and Med. **20**, 311 (1923), purified their sugar by recrystallization from alcohol.

of residue if the sample be taken immediately after preparation, but if the brew be allowed to stand several hours a mud settles out leaving a much clearer reddish solution which contains about 4.8 g of solids per 100 cc. If the combings be ground before preparing the brew, or if those obtained from the malt house are very much broken, the solids in the brew may rise as high as 6.0 g per 100 cc. without any increase in the Bios. The brew, which is acid to litmus paper, has an acidity ranging from 0.02 to 0.03 normal (sodium hydrate, litmus paper), and a pH of about 4.4. One cc. of this infusion added to 5.0 cc. of the artificial medium and 1.0 cc. of yeast suspension and made up to 10.0 cc. with water in the rocker tube, gives a count of 260 to 280, i.e. 10x270x250,000 yeast cells from the 1.0 cc. of infusion.

Concentration of the root brew: Immediately after preparation the brew is concentrated by boiling *in vacuo*, at a temperature ranging from 35°C to 50°C, to one-fourth of its volume. This treatment does not injure the Bios; for if a portion be diluted to the original volume, the yeast crop from the solution so obtained is the same as from the original brew.

Precipitation of the concentrated brew by alcohol: To the concentrate is added twice its volume of 95% alcohol, stirring meanwhile; a voluminous stringy precipitate is removed by filtration, leaving a clear reddish filtrate which contains the whole of the Bios but only two-thirds of the solids of the original brew.

II. Fractionation of Bios

The alcoholic filtrate is concentrated *in vacuo* (35°C to 50°C) to one-tenth the volume of the original root-brew, and to this *"alcohol concentrate"* is added a hot saturated aqueous solution of barium hydroxide in quantity determined as explained below; a slimy precipitate is formed which is not removed, and a strong smell of ammonia or amines is given off, moist red litmus paper held above the liquid turns blue. Alcohol, 95%, is then added in volume equal to twice the sum of the volume of the concentrate and the barium hydroxide solution; a voluminous, granular, rapidly settling precipitate is formed. In order to ascertain whether the quantity of barium hydrate added has been sufficient, a few drops of concentrated baryta water are added to a portion of the clear supernatant liquid; if there be *immediate* precipitation, more barium hydroxide is necessary.

When working with large quantities, the amount of barium hydroxide to be used should be determined by a preliminary experiment on a small scale; it depends upon the amount of solids per 100 cc. of brew, and varies from 30 to 60 g of crystalline barium hydroxide $Ba(OH)_2.8H_2O$ per litre of brew. The distribution of the barium in this reaction is given in Table VA.

The precipitate after it is filtered off is washed with dilute alcohol (2 volumes of 95% alcohol to one volume of water), and the filtrate together with the washings (*"Bios II liquor"*), is worked up for Bios II as described later.

Bios I

The barium precipitate, after washing, is stirred with three or four successive portions of water at room temperature, filtering between each; the volume of the filtrates when united should be about one-half that of the original brew. The portion of the precipitate which remians undissolved ("*barium insoluble*") on treatment with dilute sulphuric acid yields a deep red solution which contains neither Bios I nor Bios II and is consequently rejected.

Bios I liquor: The filtrates ("*Bios I liquor*") are worked up for Bios I as follows: They are first saturated with carbon dioxide, and then boiled *in vacuo* to remove the excess of the gas, after which they are filtered; the precipitate contains no Bios. To the filtrate, heated to 60°C or 70°C, is added 2.5 N sulphuric acid until no further precipitate forms, from 100 to 150 cc. of acid per litre of original brew is needed. In order to be certain that the excess of sulphuric acid is not too great, a small portion of the liquid is removed, centrifuged clear of precipitate, and concentrated baryta water added from a burette until the excess of sulphuric acid is neutralized; if the excess be large it is removed by barium hydroxide, care being taken to leave no barium in the solution; working in this manner it is possible to leave only a small excess of sulphuric acid in the liquid. The precipitate is removed by filtration, and contains no Bios.

Crude Bios I solution: The filtrate when all the barium has been removed from the Bios I liquor ("*crude Bios I solution*") is quite clear and smells sugary; it is reddish in colour and if sterilized becomes much darker. It gives very small precipitates with solutions of silver nitrate, mercuric chloride, and normal lead acetate; with phosphomolybdic acid or baryta water in the absence of alcohol there is no precipitate. The solution contains glucose; it reduces Fehling's solution; 5.0 cc. heated to 100°C for 2 hours with 0.25 cc. of phenyl-hydrazine and 0.25 cc. of glacial acetic acid, gave a bulky yellow crystalline precipitate; after washing, the crystals had a melting point of 203°C to 204°C, and were identical in crystalline form with those of glucosazone.

If a portion of the solution be diluted with distilled water to the volume of the original brew, 100 cc. of the solution so obtained contains from 1.2 to 1.8 grams of solids which is about one-third of the solids in the original brew; it is acid to litmus paper and varies from 0.02 to 0.05 normal. A "determination of Bios" in 1.0 cc. of this dilute solution gives a count of from 40 to 50 (brew gives 275), but if there be added Bios II solution (prepared as described below from the Bios II liquor obtained for 1.0 cc. of brew) the count rises to about 270. As the Bios II alone gives but a small count, these results show that Wildiers' Bios consists of two separable constituents, Bios I and Bios II, both of which must be present to enable the normal reproduction of the yeast.

The following table gives the counts obtained from 1.0 cc. of each of ten preparations of root-brew (from Dec. 1921 to Mar. 1923) and the solids per 100 cc. of each brew; also the counts obtained from solutions containing Bios I and Bios II from 1.0 cc. of the same brew. Solutions containing either the Bios I or Bios II alone give a count of 40 to 50 only.

TABLE I

Brew: Count	275	265	280	280	275	275	275	270	286	280
I & II: Count	315	336	275	275	270	250	275	286	270	260
Brew: Solids	3.35	3.16	3.56	4.56	4.73	4.73	4.47	4.71	5.70	5.32g

Precipitation of Bios I with lead: If to the *Bios I liquor* from which all the barium has been removed, there be added a solution of basic lead acetate, or a solution of neutral lead acetate followed by a solution of sodium or barium hydroxide, a precipitate is formed, the amount of which is increased on the addition of one volume of 95% alcohol; this precipitate carries down most of the Bios I, but the separation is not complete. If however, ammonia be used instead of the other alkalies, Bios I is carried down much more completely, no alcohol is necessary, and trouble due to re-solution of the precipitate by excess of alkali is avoided.

To carry out this precipitation, *Bios I liquor*, after the removal of barium by carbon dioxide and sulphuric as described above, is heated to 70°C, and the calculated amount of normal ammonia is added, viz:—enough to neutralize the acidity of the liquor and an additional amount equivalent to the acetic acid radical in the lead acetate; a solution containing 80 g of crystalized lead acetate per litre is then added in such quantity that 0.64 g of crystallized acetate is added per gram of solids in the liquor. A finely divided yellow precipitate forms which coagulates rapidly in the warm solution, and is removed while the temperature is about 70°C. The filtrate from this "*lead precipitate*" (which is much lighter in colour than Bios I liquor) on cooling deposits a small amount of bright yellow precipitate which contains no Bios I, and is therefore discarded; after removing the lead by hydrogen sulphide and the excess hydrogen sulphide by boiling *in vacuo*, this filtrate contains from 1.0 to 1.2 g of solids per 100 cc. of original brew. A Bios determination, using the amount of filtrate formed from 1.0 cc. of brew, gave a count of 60 to 100, which was only slightly increased by addition of Bios II; the filtrate thus contains but little Bios I, and an attempt to recover it by using larger quantities of lead acetate was unsuccessful.

Bios I solution: The lead precipitate, washed with boiling water (about one-tenth the volume of the brew from which it was prepared; the washings contain no Bios I) is then suspended in water at room temperature, and a current of carbon dioxide is passed through for from five to twenty minutes or longer, depending upon the amount of precipitate under treatment. A yellow solution is formed; the precipitate is removed by filtration, and is treated with carbon dioxide and water so long as the filtrates are yellow. The filtrates are united, their volume should be about one-fourth to one-half that of the original brew; they are concentrated *in vacuo* to about one-twentieth of the volume of the original brew; during this concentration a small yellow precipitate forms which contains no Bios I. Four volumes of 95% alcohol are then added, and a bulky white precipitate forms which is easily removed by filtration and contains but a trace of Bios I (after removing lead and adding excess of Bios II counts of 55, 35, 60 were obtained from the amount of the precipitate formed from 1.0 cc. of brew).

The alcoholic filtrate from this precipitate is evaporated *in vacuo* at 30°C to 50°C to a small volume and the lead removed by hydrogen sulphide (without or with previous treatment with sulphuric acid); the lead sulphide is removed by filtration, and the dissolved gas boiled off *in vacuo*. The solution thus obtained, when concentrated is reddish yellow in colour; but when diluted to the volume of the original brew used in making it, is almost colorless and perfectly clear and contains on an average from 0.10 to 0.15 g of solids per 100 cc, these include a little glucose (Fehling's solution, glucosazone); it contains about 80% of the Bios I present in the original brew (see Table II) and is almost free from Bios II. Table II gives the counts obtained from nine different preparations of Bios I solutions made in February and March 1923 from the same stock of root-brew. In each case the Bios I solution was diluted to the volume of the original brew, and 1.0 cc. of this dilute solution with 1.0 cc. of a solution of Bios II (which by itself gave a count of 50) was made up to 10 cc. with sugar, salts, and yeast suspension in the rocker tube. The original brew gave a count of 280 and contained 5.25 g of solids per 100 cc.; the solids in 100 cc. of the diluted *Bios I solution* are given in the table.

TABLE II

Count (I alone)	25	25	25	20	20	15	20	20	20
Count (I & II)	155	165	225	210	225	210	240	200	220
Solids in I	0.14	0.16	0.12	0.08	0.11	0.11	0.18	0.17	0.10

Bios II

Two methods of purifying *Bios II liquor* have been tried, only one of which is here described. The second method (in which alcohol was used) was worked out in the hope of avoiding the large expenditure of acetone involved in the first, but does not give so pure a product. In the acetone method, which was first employed, the *Bios II liquor* is saturated with carbon dioxide, the excess carbon dioxide removed by boiling *in vacuo*, and the precipitate (which contains no Bios II) filtered off[1]. The filtrate, after removing the alcohol and diluting to the volume of the original brew, is alkaline (about 0.02 normal; hydrochloric acid, litmus paper); it contains 1.0 to 1.2 g of solids per 100 cc. of brew. This filtrate is now evaporated *in vacuo* at as low temperature as possible until large bubbles are formed which completely fill the vessel; this occurs when the volume has been reduced to about one-tenth or one-fifteenth that of the original brew. If acetone be added to this concentrate, a milkiness is formed, which at first disappears on shaking; on further addition of acetone a heavy red oily liquid separates; on still further addition

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[1] It has been found that in some cases the carbon dioxide does not remove all the barium. A test should be made with sulphuric acid to see if a trace of barium remains; if so, it must be removed with sulphuric acid before counts or solids are determined.

of acetone with violent shaking, this liquid is replaced by a layer of yellowish gum (*"acetone precipitate"*), which adheres to the walls of the vessel and contains but little Bios II; the addition of acetone must be continued until no further precipitation takes place (from 0.8 to 1.5 times the volume of the original brew). The yellow acetone solution is decanted off, filtered if necessary, the precipitate washed with acetone and the washings added to the solution; this is now concentrated *in vacuo* until the reddish yellow residue is almost the consistency of a gum; this residue is extracted with successive portions of warm acetone (in all, about one-half the volume of the original brew); the undissolved portion *"acetone gum"*, contains but little Bios II. The acetone is evaporated *in vacuo*, leaving a thick, reddish liquid, of peculiar nauseating odor; on addition of water, in volume equal to that of original brew, a turbid yellowish liquid results which cannot be cleared by filtration (*"Bios II solution acetone"*). This liquid contains about 0.10 g of solids, nearly all organic, per 100 cc. of brew; it is bitter and is alkaline to litmus paper (about 0.004 N), and contains from 80% to 90% of the Bios II in the original brew.

The "acetone precipitate" and "acetone gum" were dissolved in a little water, traces of acetone removed by boiling *in vacuo*, and the solution made up to the volume of the original brew. This solution has a peculiar, penetrating odor, distinct from that of the "Bios II solution acetone"; it is alkaline to litmus (about 0.01 N), and contains about 1.0 g of solids per 100 cc. of brew including a trace of Bios II, (see Table III). The following table gives the counts from five preparations made in April and May 1922, also the solids in 100 cc. of "Bios II solution acetone" after diluting to the volume of the brew from which it was prepared. The quantities used were those from 1.0 cc. root-brew; the last two lines are duplicate determinations with the same preparations. The precipitate and the gum are evidently free from Bios.

TABLE III

Col. 1 *Bios II solution acetone.*

Col. 2 Acetone precipitate and acetone gum.

Col. 3 *Bios II solution acetone*, acetone precipitate, and acetone gum.

Col. 4 *Bios II solution acetone* and a *crude Bios I solution* which by itself gave a count of 50.

Col. 5 *Bios II solution acetone*, acetone precipitate, acetone gum and *crude Bios I solution*, which by itself gave a count of 50.

Col. 6 Grams of solids in 100 cc. *Bios II solution acetone.*

No.	1	2	3	4	5	6
1	35-50	50-75	75	275	285	0.11
2	35-50	50-75	75	275	340	0.11
3	50	50-75	50-75	250	256	0.22
4	50	50-75	——	270	275	0.08
5	50	50-75	——	275	286	0.078
5	35-50	50-75	——	275	280	0.10

Degree of Concentration Attained

The count obtained after 24 hours in the rocker tube, multiplied by 2,500,000 gives the number of yeast cells produced from the 1.0 cc. of solution experimented with; and if this product be divided by the number of grams of solids in 1.0 cc. the quotient gives the number of cells produced per gram of solids in the preparation. The figures in Table IV if multiplied by 10^{10} give the results of such calculations based on the data of Table IV lines 1 and 3 for the Brew, Table II lines 2 and 3 for the Bios I solution, and Table III, Cols. 4 and 6, for the Bios II solution. In the experiments with Bios I it was of course necessary to add an excess of Bios II to the salts and sugar in the tube and *vice versa;* no correction was necessary for the amount of Bios II added with the Bios I used as reagent, but the Bios II solutions were not so pure and by themselves (with salts and sugar) gave a count of about 50, this has been allowed for in the calculations of Table IV.

TABLE IV

Brew:	2.0	2.1	2.0	1.5	1.4	1.4	1.5	1.4	1.3	1.3
Bios I solution:	19	18	36	50	40	37				
Bios II solution:	51	51	23	69	72	56				

Distribution of the Solids

Table V shows the distribution of the solids originally contained in the alcohol concentrate prepared from 100 cc. of brew.

TABLE V

Col. 1 Grams of solids in the alcohol concentrate from 100 cc. of brew.
Col. 2 Total grams of solids, excluding barium, in the fractions (sum of Cols. 3-5).
Col. 3 Grams of solids in *Bios I liquor* from 100 cc. of brew after subtracting the weight of the barium in the Bios I liquor.
Col. 4 Grams of solids in *Bios II liquor* from 100 cc. brew after subtracting the barium.
Col. 5 Grams of solids in "*barium insoluble*" after subtracting the barium.

No.	1	2	3	4	5
1	3.02	3.24	0.96	1.93	0.35
2	3.02	2.96	1.24	1.26	0.46
3	3.02	2.96	1.27	1.17	0.52
4	3.02	3.02	1.13	1.41	0.48
5	3.02	2.98	1.01	1.46	0.52

Distribution of the Barium

Table VA shows the distribution of the barium in an experiment in which varying amounts of barium hydroxide were added to an *alcohol concentrate* (see page 1184); when more than 4.5 g of crystallized hydroxide were used per 100 cc. of original brew, the excess separated from the alcoholic solution in crystalline form mixed with the barium precipitate.

TABLE Va

The weights refer to 100 cc. of original root-brew; the numbers 1, 2, 3 etc., refer to the same experiments as 1, 2, 3 etc., of Table V.

Col. 1 Grams of $Ba(OH)_2.8H_2O$ used.
Col. 2 Grams of Ba used (calculated from Col. 1).
Col. 3 Total grams of Ba found (sum of Cols. 4-8).
Col. 4 Grams of Ba in the CO_2 precipitate from *Bios I liquor.*
Col. 5 Grams of Ba remaining in *Bios I liquor* after precipitation by CO_2.
Col. 6 Grams of Ba in the CO_2 precipitate from *Bios II liquor.*
Col. 7 Grams of Ba remaining in *Bios II liquor* after precipitation by CO_2.
Col. 8 Grams of Ba in *barium insoluble.*

No.	1	2	3	4	5	6	7	8
1	2.56	1.098	1.124	0.106	0.384	0.233	0.000	0.401
2	4.50	1.938	1.896	0.473	0.409	0.380	0.102	0.532
3	6.41	2.762	2.796	1.007	0.435	0.702	0.038	0.614
4	6.41	2.762	2.562	0.906	0.409	0.657	0.038	0.552
5	9.62	4.144	3.837	2.056	0.416	0.710	0.051	0.604

III. Comparison of Two Strains of Yeast

Of the two yeast cultures brought to Toronto by Prof. W. H. Eddy, both originating from Fleischmann's yeast cake, the first proved very like the strain that we have used here for years; the second was a top yeast[1]. To compare them, tubes were prepared containing (*a*) salts and sugar alone, (*b*) salts and sugar and Bios I, (*c*) salts and sugar and Bios II, (*d*) salts and sugar, Bios I and Bios II. The Bios I employed was a very pure preparation made by Mr. Sims, and only 0.05 mg. of it was added to the 10 cc. of medium in tubes *b* and *d;* the Bios II was the best I could find ready to hand, the results with tubes *c* and *d* show that it was not so pure as the *Bios II acetone* of Table III. Table VI gives the counts observed after 36 hours and after 200 hours in the rocker tube at 25°C; the initial count was unity.

TABLE VI

	36 Hours			200 Hours		
	Prof. Eddy's Bottom Yeast	Our Bottom Y.	Top Y.	Prof. Eddy's Bottom Yeast	Our Bottom Y.	Top Y.
a no Bios	8	10	900	35	85	3800
b Bios I	10	20	990	50	95	3950
c Bios II	85	85	1700	205	270	5100
d I and II	325	375	1770	325	375	5100

It is obvious that while the reproduction of this top yeast is much helped by addition of the two Bioses, or indeed by addition of either one of them, yet even in the absence of Bios it gives a larger crop in 36 hours than the

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[1] Wildiers used "une levûre haute du type *Sacch. cerev. I Hansen*" (loc. cit.)

bottom yeast does when both Bioses are present. The much discussed question whether Bios is indispensable or not to the reproduction of "yeast" is therefore ambiguous; the particular strain of yeast employed in the experiment makes all the difference.

I plated some of this top yeast on wort agar; the colonies are quite distinct 24 hours after seeding, when those of the bottom yeast are hardly visible. The appearance of the colonies is also quite different; instead of a three- or four-pronged star there is a raised dot in the centre of each. Grown in wort, the top yeast forms a scum on the surface, the other a sediment. Under the microscope the cells of the top yeast are much smaller than those of the other; measurements with the haemocytometer and the centrifuge tube show that the volume of a top yeast cell is very close to one-half that of a bottom yeast cell.

IV. Animal Experiments

In these experiments comparison was made between the action of my Bios I and Bios II preparations on the one hand, and such quantities of rice polishings, malt combings, yeast, or orange juice (or preparations made from them) as contained approximately the same quantity of the Bioses, on the other.

Determination of Bios in rice polishings, etc,: 300 g of the polishings was extracted for 24 hours at 55°C with 3 litres of water, and 2660 cc. of filtrate obtained which contained 1.27 g solids per 100 cc. The residue was extracted a second time with 2 litres of water (24 hours at 55°C) and yielded 2010 cc. of a filtrate containing 0.40 g solids per 100 cc. The two filtrates were united. In the rocker tube (24 hours at 25°C, initial count $C = 1$).

1.0 cc. filtrates + salts and sugar gave a count of..... 210
1.0 cc. filtrates + salts and sugar + excess Bios II.... 200
1.0 cc. filtrates + salts and sugar + excess Bios I..... 310

Hence the Bios I obtained from one gram of rice polishings is sufficient to give a crop of $4670/300 \times 2,500,000 \times 210 = 80 \times 10^8$ yeast cells, while the Bios II in one gram is sufficient for 120×10^8 cells.

Similar experiments with the other materials gave the following results:

TABLE VII

	Bios I	Bios II
1.0 g. rice polishings	80×10^8	120×10^8
1.0 g. dried brewer's yeast	160×10^8	260×10^8
1.0 g. malt combings	140×10^8	95×10^8
1.0 cc. root-brew	9×10^8	7.5×10^8
1.0 cc. orange juice	12×10^8	7.5×10^8
1.0 cc. Bios I solution	6×10^8	——
1.0 cc. Bios II solution	——	6×10^8

Pigeons

The birds were bought in a poultry market and were of various ages and weights. Each of the first lot of 13 pigeons was given 10 g. of polished rice daily (forced feeding being necessary after the first four days) and, in addition, Bios preparations equivalent to 0.6 g. rice polishings; these consisted of Bios I solution, Bios II solution, both Bios I and Bios II, root-brew, or dry malt combings; one of the birds received 0.6 g. of rice polishings per day, and two nothing but the rice. The birds were weighed once a week, and a chart kept of each. With the exception of the bird supplied with rice polishings, who lost weight, all got polyneuritis; two of them were cured by administering rice polishings on the fourteenth or fifteenth day, the first of these received 1.0 g. and recovered slowly, the other received 0.8 g. followed by 1.0 g. on the next day and recovered more rapidly.

The second lot (12 birds) were given larger amounts of the Bios preparations, viz. those corresponding to 3.0 g. of rice polishings per day; the solutions employed were evaporated to a small bulk and administered by means of a pipette. The birds were grouped in pairs, one of each pair being fed one-twentieth of its body weight of polished rice daily, the other one-twentieth of an artificial diet[1]. In this case again the birds that received rice polishings escaped polyneuritis. Two birds were given 3 g. polishings daily for 14 days and then 3 g. combings; 20 days after this change, one (art. diet) developed the disease, the other (rice) escaped. Of two pigeons each receiving Bios I solution, one (art. diet), got polyneuritis in 17 days, the other (rice) escaped and was still alive but very weak after 45 days. Both birds on Bios II developed the disease in 22 days (rice) and 27 days (art. diet) respectively, while one (art. diet) to which no Bios was given fell ill in 22 days. Of the two birds receiving both Bios I and Bios II, one (rice) got polyneuritis in 22 days, the other (art. diet) was still free from the symtoms on the 24th day when its crop burst and it had to be chloroformed. Concentrated root-brew was given to three; this preparation was sticky, and difficulty in its administration caused the death of two of them, the third (rice) lived 45 days without polyneuritis but in very poor condition.

It seems abundantly evident from these results that administration of the Bioses in quantities equivalent to those in 0.6 g. or 3.0 g. of rice polishings in no way replaces the latter as a preventative of or a cure for polyneuritis. Polished rice seems to be less harmful than the artificial diet employed; it may be that Bios I helps a little, but vastly less than the quantity of rice polishings that with Bios II gives the same yeast crop. The Bios II solution was very distasteful to the birds, a little sugar helped it down, but its curative value was *nil*.

Guinea Pigs

The pigs were fed on a diet of oats, hay, and carrots *ad. lib.* until they weighed about 300 g. after which they were put on a scorbutic diet consisting of: oats, sound whole grains ground in the laboratory, 59%; klim, heated

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[1] 22% casein (heated for 24 hours at 120°C), 33% starch, 10% cane sugar, 2% agar-agar, 30% butter fat, and 3% of a mixture of salts consisting of:—sodium chloride, 46.25; magnesium sulphate cryst., 71.20; mono-sodium phosphate, 92.68; di-potassium phosphate, 254.60; calcium acid phosphate, 144.20; calcium lactate, 347.00; ferric citrate, 31.52; sodium fluoride, 0.55; maganese sulphate cryst., 2.00; potassium iodide, 10.00; parts by weight.

in shallow trays in the oven at 110°C for at least 4 hours, 30%; butter fat, prepared by melting butter at a low temperature and decanting the fat, 10%; sodium chloride, 1%.

The diet was administered for 18 days, during the first few of which carrots were supplied in addition. On the 18th day administration of the Bios preparations was begun.

One pig received 5.0 cc. of orange juice daily, this is the only one that escaped scurvy. One received no Bios, one received one gram of malt combings daily (about twice the Bios of the 5.0 cc. orange juice). One received a solution of Bios I containing about twice the amount in the 5.0 cc. orange juice. One a solution of Bios II containing 1.8 the amount in the 5.0 cc. orange juice, and one both the Bioses in the same amounts as given to the two other animals.

A full account of the details of these experiments has been published by Miss J. Deas[1]; the above summary is sufficient to show that my preparations are distinct from vitamin C.

Rats

Young, healthy, growing rats weighing about 30 g. were used; they were caged individually, weighed every few days, and their weights charted.

The basal diet consisted of: casein (heated for 24 hours at 120°C), 18%; starch, 58%; lard (aerated), 15%; salt mixture (same as used with the pigeons), 4%; agar-agar, 5%; with 5.6 mg. codliver oil per rat daily.

The weight of dried brewers' yeast necessary to provide ample vitamin B for growth in young rats is 0.4 g. per day; the amount of Bios I and Bios II in the various preparations used to replace it are given in Table 8 (in which the factor 10^8 is omitted); the liquids were concentrated to 0.3-0.5 cc. and administered through a tuberculin syringe fitted with a soft rubber tip.

TABLE VIII

	0.4 g. dried yeast	1.0 g. combings	1.0 g. rice polishings	8.5 cc. brew	11 cc. Bios I sol.	18 cc. Bios II sol.
Bios I	64	140	80	76	66	—
Bios II	104	95	120	64	—	108

Twenty-four rats were used ("group *A*"); two fed on a normal diet increased in weight from 30 g. to 100 g. and 90 g. respectively in 30 days, i.e. about 2.0 g. daily; seven died; the remaining fifteen were placed on the basal diet until their weights fell off, the Bios preparations were then added to the basal diet, and finally rice polishings were supplied as a check and a cure. Of the fifteen, three each were given malt combings, root-brew, Bios I, Bios II, and both Bios I and II together respectively. In every case the rats lost weight when their diet consisted of the basal diet (including codliver oil) either alone or with Bios preparations, but gained when one gram per day of rice polishings was supplied. Full details of these experiments are being

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[1] J. Biol. Chem. 61, 5 (1924).

published by Miss J. Deas[1]; Table IX gives the record of Rat No. 51 as example; under T is given the time in days from the beginning of the chart, W is the weight in grams of the rat, under $\Delta W/\Delta T$ the gain in weight per day, and under *F* the diet viz: *N* = normal diet, *B* = basal diet alone. *P* = basal diet plus Bios preparations, *R* = basal diet plus rice polishings; an asterisk shews the date at which the administration of codliver oil was begun.

TABLE IX

T	W	ΔW/ΔT	F	T	W	ΔW/ΔT	F	T	W	ΔW/ΔT	F
0	32	2.0	N	32	42	−0.3	P	60	57	−0.3	P
4	40	1.0	B	35	43	0	P	63	56	−1.6	P
8	44	0.7	B	37	43	−1.0	P	65	53	+0.5	R
11	46	1.0	B	39	41	+4.0	R	67	54	+1.3	R
14	49	0.	B	42	52	+1.5	R	70	58	+1.0	R
16	49	0.5	B	44	55	+1.5	R	72	60	+1.0	R
18	50	−0.7	B	46	58	+1.0	B	74	62	+0.3	R
21	48	−0.5	B	49	61	0	B	77	63	+1.0	R
23*	47	0	B	51	61	0	B	78	64		R
25	47	−0.3	B	53	61	−0.7	P				
28	46	−0.5	P	56	59	−1.5	P				
30	45	−1.5	P	59	57	0	P				

V. An Attempt to fractionate the Growth-Promoting Vitamin

In the course of the experiments with the rats of Group *A*, the infusion of rice polishings described on page 1191 was administered daily (in the quantity prepared from one gram of polishings) to nine of the rats and proved ineffective; as administration of one gram of the polishings themselves invariably produced prompt results, it was sought to determine the conditions under which an effective infusion can be prepared, and experiments were made with infusions in water at two temperatures, in aqueous alcohol, and in alkaline and acid solutions with or without addition of trypsin or pepsin respectively. The rats used in this work were all from the same importation; some of them ("group *B*") were large enough for use when they arrived, the others ("group *C*") were from litters raised in the laboratory. None of them were as suitable for the work in hand as those of group *A*; the group *B* rats proved capable of gaining weight on the basal diet, and those of group *C* remained stationary or lost but little. However, the results seem definite enough to warrant publication.

Comparison of the Infusions

Water:—A new infusion made at 55°C as described on page 1191 was administered (each day the quantity from one gram of polishings) to each of eight rats; when these were put on the basal diet (including codliver oil), the after-effect of the normal diet was perceptible on the charts for about a week or ten days, after which they were continued on the basal diet a fort-

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[1] J. Biol. Chem. 61, 5 (1924).

night or longer before the infusion was added to their diet. Table X gives the number of days on the basal diet after the effect of the normal diet had worn off, and the gain in weight during that period; also the number of days and the gain per day while they were receiving the infusion.

TABLE X

Group		B	B	C	C	C	C	C	C
Basal diet:	Days	42	42	14	14	14	14	14	14
" "	Gain	30	32	0	2	0	0	0	3
" "	$\Delta W/\Delta T$	0.7	0.7	0	0.1	0	0	0	0.2
Infusion	Days	30	30	20	20	20	20	20	20
"	Gain	42	42	22	20	11	4	0	8
"	$\Delta W/\Delta T$	1.4	1.4	1.0	1.0	0.5	0.3	0	0.4

A third infusion was made in similar manner but at 37°C. for 12 hours, using three portions each of 500 cc. water, and 100 g. polishings, each extraction lasted 12 hours, and a few drops of chloroform were added as protection against microbes. The quantity prepared from 1.0 g. of polishings was given daily to each of three rats, and one gram of the dried residue from the extraction to each of two others (all five of group B); from the results of Table XI, it seems that at least half the vitamin must have been left in the residue.

TABLE XI. (*Water*). *I*, infusion; *R*, residue; Rats *B*.

Basal diet:	Days		28	28	28		32	32
"	$\Delta W/\Delta T$		1.0	0.8	0.4		0.6	0.6
Preparation	Days	*I*	20	20	20	*R*	20	20
"	$\Delta W/\Delta T$		1.1	1.3	0.6		1.7	1.0

Alcohol: 300 cc. of 95% alcohol diluted to 500 cc. with water was used to replace the water of the previous paragraph, the 100 g. of polishings being extracted three times for 12 hours at 37°C as before. On evaporating the mixed filtrates a fatty precipitate (soluble in alcohol) was formed, this was not removed; 0.5 cc. of the concentrated infusion corresponded to one gram of the polishings. Table XII shows that much of the vitamin stays in the residue.

TABLE XII. (*Alcohol*). *I*, infusion, 0.5 cc.; *R*, residue, 1.0 g.; (daily). Rats *B*.

Basal diet:	Days		28	28	28		28	28
"	$\Delta W/\Delta T$		0.6	0.6	0.4		0.6	0.8
Preparation:	Days	*I*	24	24	24	*R*	24	24
"	$\Delta W/\Delta T$		0.4	0.6	1.5		1.2	1.3

Trypsin: 500 cc. of a solution containing 2.0 g. of trypsin[1], 1.5 g. of sodium bicarbonate, and 7.0 cc. of N/10 hydrochloric acid (to bring it to PH=8) was used to extract 100 g. rice polishings, a few drops of chloroform being added to keep down bacteria. After 12 hours at 37°C an attempt was made to filter, but only 250 cc. of filtrate was obtained. One litre of the bicarbonate-trypsin-solution together with 3.0 g. additional trypsin was added to the residue; and after another 12 hours at 37°C 1160 cc. of filtrate was obtained which was added to the first 250 cc. and the whole brought to the boiling point to destroy the trypsin. Nine-tenths of this liquid was then evaporated *in vacuo* (at about 50°C) to a volume of 100 cc. (a small precipitate formed during the evaporation was not removed) and to the concentrate was added 60 cc. of 95% alcohol; this caused a white precipitate *"alcohol precipitate"* which was removed by filtration and washed with 60% alcohol, after drying in the air it weighed 2.5 g. The filtrate was evaporated to 45 cc. so that 0.5 cc. corresponded to 1.0 g. of the polishings. The results of Table XIII show that the vitamin is distributed among the fractions; and in a parallel set of experiments in which the sodium bicarbonate solution was used without trypsin, much the same result was obtained (Table XIV).

TABLE XIII. (*Trypsin*). *F*, filtrate, 0.5 cc. *R*, residue, 1.0 g.; *P*, alc. ppte., 0.1 g; (daily). Rats *B*.

Basal diet:	Days	38	36	34	34	34	42
"	ΔW/ΔT	0.5	0.8	0.6	0.8	0.9	0.6
Preparation:	Days	*F* 14	14	16	*R* 16	18	*P* 18
"	ΔW/ΔT	1.8	0.8	0.6	1.2	1.1	0.8

TABLE XIV. (*Bicarbonate*). *F*, filtrate 0.5 cc.; *R*, residue, 1.0 g.; *P*, alc. ppte., 0.1 g; (daily). Rats *B*.

Basal diet:	Days	22	22	22	22	22	22
"	ΔW/ΔT	0.7	0.2	0.8	0.8	0.8	0.6
Preparation:	Days	*F* 16	17	16	*R* 16	*P* 12	15
"	ΔW/ΔT	1.5	1.7	1.3	2.0	−0.5	1.7

Pepsin: 100 g. of rice polishing was extracted with 500 cc. 0.6 *N* hydrochloric acid containing 0.5 g. pepsin[2] for 12 hours at 37°C; the residue was extracted twice more in the same manner and the filtrates united, neutralized with sodium bicarbonate, evaporated *in vacuo*, and treated with alcohol as in the case of the trypsin infusion. The precipitate with alcohol weighed 4.5 g. air-dried; the administration of 0.1 g. daily helped growth (Table XV), but in the case of a second preparation made on the large scale, where the

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[1] Trypsin—Digestive Ferments Co., Detroit, Mich.

[2] *"Pepsinum"*—National Drug and Chemical Company of Canada Limited, Pharmaceutical Laboratory, Montreal.

precipitate was thoroughly washed with 60% alcohol, even quantities of 0.25 to 1.0 g. daily proved ineffective (Table XIX). The residue after extraction with the pepsin solution likewise proved unable to maintain growth (Tables XV and XVIII) so digestion with pepsin evidently concentrates the vitamin in the alcohol filtrate. The filtrate was concentrated *in vacuo* until 0.5 cc. corresponded to 1.0 g. of polishings.

Parallel experiments in which the hydrochloric acid alone was employed (without pepsin), left a considerable amount of the vitamin in the residue (Table XVI).

TABLE XV. (*Pepsin*). *F*, filtrate, 0.5 cc.; *R*, residue, 1.0 g; *P*, alc. ppte., 0.1 g; (daily). Rats *B*.

Basal diet:	Days	22	22	22	22	22	22	22
"	ΔW/ΔT	0.3	0.8	0.5	0.6	0.5	0.2	0.5
Preparation:	Days	*F* 18	20	16	*R* 14	14	*P* 20	16
"	ΔW/ΔT	2.2	1.4	1.3	0.2	0	1.9	0.8

TABLE XVI. (*Acid.*) *F*, *R*, *P*, *Rats*, as in Table XV.

Basal diet:	Days	22	22	22	22	22	22
"	ΔW/ΔT	0.4	0	0.3	0.1	0.7	0.5
Preparation:	Days	*F* 18	20	20	*R* 24	20	*P* 14
"	ΔW/ΔT	1.1	0.7	0.9	0.9	1.5	−0.2

Treatment of the Pepsin Infusion with Alcohol and Baryta

The above results show that digestion with pepsin is the best way to remove the vitamin from rice polishings; accordingly 2750 g. of the polishings were treated as described above, and the neutralized filtrate evaporated to 5900 cc.; to this was added 12 litres of 95% alcohol; after it had stood for a week to settle, the precipitate was removed by a Sharples centrifuge and washed twice with dilute alcohol. The precipitate (244 g. air dried) contained very little vitamin (Table XIX), and the residue from the extraction practically none (Table XVIII). The solution was evaporated *in vacuo* to a volume of 2500 cc. and 5 litres of 95% alcohol was added, only a trace of precipitate being formed; the volume was now 7310 cc. or 2.66 cc. per gram of polishings used. Amounts of this solution (after freeing from alcohol by evaporation) which corresponded to 0.25, 0.50, 0.75 and 1.0 g. rice polishings were then given daily to 16 rats (4 for each amount, Table XVII), and, for comparison, 0.25, 0.50, 0.75 and 1.0 g. of rice polishings themselves to fourteen more (Table XX).

Comparison of Tables XVII and XX shews that the filtrate is somewhat inferior to the polishings from which it was prepared; and that, between 0.5 and 1.0 g., the amount supplied to the rats is unimportant.

TABLE XVII. (*Pepsin.*) Filtrate from *a* 0.25 g; *b* 0.50 g; *c* 0.75 g; *d* 1.0 g; (daily). Rats *C*.

Basal diet:	Days	10	10	10	6	10	10	10	12
"	$\Delta W/\Delta T$	0.2	0.2	0.2	−0.7	0	−0.2	0.2	0
Filtrate:	Days	*a* 20	20	20	20	*b* 20	20	20	20
"	$\Delta W/\Delta T$	0.5	0.5	0	0.8	0.8	0.7	1.1	0.7
Basal diet:	Days	10	8	10	8	10	10	10	
"	$\Delta W/\Delta T$	−0.6	−0.6	0	0.7	0.2	0.2	−0.6	
Filtrate:	Days	*c* 20	20	20	*d* 20	20	20	20	
"	$\Delta W/\Delta T$	0.8	0.6	0.8	0.8	0.9	0.8	0.8	

TABLE XVIII. (*Pepsin.*) Residue: *a* 0.25 g; *b* 0.50 g; *d* 1.0 g; (daily). Rats *C*.

Basal diet:	Days	14	14	14	14	14	14	14	14
"	$\Delta W/\Delta T$	0.3	0.7	0.8	0.4	0.2	0.3	0.3	0.6
Residue	Days	*a* 16	16	*b* 16	16	16	*d* 16	16	16
"	$\Delta W/\Delta T$	0.5	0.3	0	0.3	0	0	0	0

TABLE XIX. (*Pepsin.*) Alc. precip: *a* 0.25 g; *b* 0.50 g; *d* 1.0 g; (daily). Rats *C*.

Basal diet:	Days	18	18	17	16	16	16
"	$\Delta W/\Delta T$	0.5	0.7	0	0.1	0.1	−0.3
Precipitate:	Days	*a* 14	14	*b* 14	14	*d* 14	14
"	$\Delta W/\Delta T$	0.3	0.7	0.6	0.6	0.6	0.3

TABLE XX. (*Polishings.*) *a* 0.25 g; *b* 0.50 g; *c* 0.75 g; *d* 1.0 g; (daily). Rats *C*.

Basal diet:	Days	10	12	12	12	12	10	10	12
"	$\Delta W/\Delta T$	0.2	0.3	0.1	0.3	−0.3	0.2	0.2	−0.1
Polishings:	Days	*a* 30	30	30	30	*b* 30	30	30	30
"	$\Delta W/\Delta T$	0.4	0.5	0.5	0.3	0.7	0.5	0.5	0.6
Basal diet:	Days	10	10	12	10	10	14		
"	$\Delta W/\Delta T$	−0.4	−0.3	0	−0.2	0	−0.3		
Polishings:	Days	*c* 30	30	30	*d* 30	30	30		
"	$\Delta W/\Delta T$	0.7	0.8	0.9	0.8	0.6	0.8		

Treatment with baryta: To 667 cc. of the 7310 cc. of solution (*i.e.* to the solution from 250 g. of polishings) was added 100 g. crystallized barium hydroxide dissolved in 100 cc. of boiling water (the amount being based on previous work in which the two Bioses were obtained from an aqueous solution of the polishings); 300 cc. of 95% alcohol was then added, and after assuring myself that no more baryta was necessary, the precipitate was removed by filtration, washed with 60% alcohol and treated with water etc., as described under "Bios I," ultimately obtaining 125 cc. of a solution corresponding to the "*Crude Bios I solution*" of page 1185 and containing 13.6 g. of solids.

The amounts of Bios I and Bios II in 0.05 cc. of this solution were determined in the rocker tube; the counts were:—alone, count of 45; with excess Bios I, count of 53; with excess Bios II, count of 415. The results with rats (Table XXI) shew that it contained no vitamin.

TABLE XXI. (*Bios I solution.*) 0.5 cc. solution (from 1.0 g. polishings).
Rats *C.*

Basal diet:	Days	8	8	8	8
"	$\Delta W/\Delta T$	−0.5	0	0	−0.3
Solution	Days	20	20	20	20
"	$\Delta W/\Delta T$	0.1	−0.1	0	−0.1

The filtrate was freed from barium and alcohol as described under "*Bios I liquor,*" and brought to a volume of 125 cc., which contained 40 g. of solids. In the rocker tube 0.05 cc. gave alone a count of 75; with excess Bios I, a count of 205; with excess Bios II, a count of 85; it therefore contains a little Bios I and a large amount of Bios II. The results with rats (Table XXII) shew that it was free of vitamin, and those of Table XXIII shew that the two solutions administered together were unable to maintain growth.

TABLE XXII. (*Bios II solution.*) 0.5 cc. solution (from 1.0 g. polishings).
Rats *C.*

Basal diet:	Days	8	8	8	8
"	$\Delta W/\Delta T$	0	−0.7	−0.3	+0.3
Solution	Days	20	20	20	20
"	$\Delta W/\Delta T$	0	0	0.1	0

TABLE XXIII. (*Bios I and II solutions.*) Amounts from 1.0 g. polishings.
Rats *C.*

Basal diet:	Days	8	8	8	8
"	$\Delta W/\Delta T$	0.3	−0.3	−0.3	0
Solutions:	Days	20	20	20	20
"	$\Delta W/\Delta T$	0.2	0	0.2	0

The portion of the barium precipitate that remained undissolved (corresponding to the "*barium insoluble*" from the combings) was left with 130 cc. of cold 1.25 *N* sulphuric acid over night, filtered, neutralized with baryta and evaporated *in vacuo* to 100 cc. Table XXIV gives the results when 0.5 cc. of this solution was administered daily; it evidently contains no vitamin.

TABLE XXIV. 0.5 cc. solution prepared from the "*barium insoluble.*"
Rats *C.*

Basal diet:	Days	8	8	8	8
"	$\Delta W/\Delta T$	0	−0.5	−0.5	−0.5
Solution:	Days	20	20	20	20
"	$\Delta W/\Delta T$	0.2	0	died	0.2

Evidently nothing has occurred with the vitamin analogous to the fractionation of the Bios; on the contrary it is mostly destroyed by the process.

Summary

1. By precipitation with baryta in alcoholic solution, the Bios contained in malt combings and in rice polishings can be fractionated into Bios I and Bios II, neither of which by itself has any great influence on the rate of reproduction of *saccharomyces cerevisiae* Race F, but which if both are present together enormously increase the crop of yeast.
2. The effect of these substances on the rate of reproduction of yeast depends on the strain of yeast experimented with; a top yeast is described which is much less dependent on Bios than *Race F.*
3. Neither Bios I nor Bios II nor both together can replace the vitamins in preventing polyneuritis in pigeons or scurvy in guinea pigs or in maintaining the growth of rats.
4. A method for extracting the growth-promoting vitamin from rice polishings is described.
5. The chemical procedure that results in the fractionation of Bios destroys the growth-promoting vitamin without fractionating it.

My thanks are due to Professor W. Lash Miller under whose direction this research was carried out, to Miss J. Deas for collaboration with the guinea pigs and rats, to Miss J. Panton and Miss F. Burwash for assistance in feeding the pigeons and to Mr. S. W. Davidson and Mrs. G. H. W. Lucas for much help with the preparations.

The University of Toronto,
August, 1924.

A STUDY OF THE MECHANISM OF THE CATALYTIC DECOMPOSITION OF ETHYL ACETATE BY NICKEL AT VARIOUS ELEVATED TEMPERATURES

J. N. PEARCE AND C. N. OTT

The catalytic properties of finely divided nickel recently reduced from its oxide were first noted by Sabatier about 1880. He and his co-workers, and others have since made many additional discoveries of uses for nickel prepared in this way. Perhaps the most important of the uses are met with in the hydrogenation of unsaturated organic compounds. Nickel may also act catalytically as a dehydrogenating or as a decomposing agent under proper conditions.

Bancroft[1] states that when ethyl acetate is passed over nickel carbon dioxide and propane are formed. He states that the reaction is probably not complete, but he does not state the temperature at which this reaction takes place. He further points out the lack of knowledge of the exact mechanism of the reaction, and he suggests that hydrogen be mixed with the ethyl acetate so that the hydrogen might react with the decomposition products before they have the opportunity to react with each other. Sabatier and Mailhe[2] have shown that aliphatic acids in contact with nickel break up chiefly in two ways. The first consists in the elimination of carbon dioxide from one molecule of the acid; in the second, there is an elimination of water and carbon dioxide from two molecules of acid:

$$(1)\quad RCOOH \longrightarrow CO_2 + RH, \text{ and}$$
$$(2)\quad 2RCOOH \longrightarrow RCOR + H_2O.$$

Sabatier and Senderens[3] state that acetone is decomposed rapidly by nickel at 270° to give carbon monoxide, methane, hydrogen, carbon, and a little ethane and ethylene. They have also shown that ethyl alcohol is rapidly decomposed by nickel above 230° to give acetaldehyde and hydrogen, and further that above 330° the aldehyde is completely decomposed into methane and carbon monoxide. Methyl alcohol is found to be slowly decomposed by nickel at 180°, and rapidly at 250° into formaldehyde and carbon monoxide. At 250° and above, however, part of the formaldehyde is destroyed, and at 350° the resulting gas is a mixture of methane and carbon dioxide. These same authors[4] report that ethyl ether when hydrogenated over nickel gives methane and carbon monoxide. Sabatier and Mailhe[5] have found that ethyl formate is decomposed by nickel to give chiefly carbon monoxide and alcohol; the latter decomposes still farther into aldehyde,

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[1] Sabatier-Reed: "Catalysis in Organic Chemistry," 180 (1922).
[2] Sabatier and Mailhe: Compt. rend., **52**, 1212 (1911).
[3] Sabatier and Senderens: Ann. Chim. Phys., (8) **4**, 474 (1905).
[4] Sabatier and Senderens: Bull., (3) **33**, 616 (1905).
[5] Sabatier and Mailhe: Compt. rend., **154**, 49 (1912).

methane and carbon monoxide. Mond[1] found that reduced nickel at temperatures between 350° and 450° can produce the reaction: $2CO \longrightarrow CO_2+C$. Sabatier and Senderens[2] have shown, however, that this reaction begins at 230° and is complete above 350°.

Theoretically, the decomposition of ethyl acetate might take place in one or more of several ways. It might give the CH_3 and $COOC_2H_5$ radicles, in which case the addition of hydrogen should lead to the formation of CH_4 and ethyl formate, or its reduction products, and possibly some ethane:

(1) $CH_3COOC_2H_5 \longrightarrow CH_3- \ + \ -COOC_2H_5$, or with hydrogen
$CH_3COOC_2H_5+H_2 \longrightarrow CH_4+HCOOC_2H_5$.

It might break up to give first the ethyl and acetate radicles which form ethane and acetic acid, or its reduction products, if hydrogen were added:

(2) $CH_3COOC_2H_5 \longrightarrow CH_3COO- \ + \ -C_2H_5$, or with hydrogen
$CH_3COOC_2H_5+H_2 \longrightarrow CH_3COOH+C_2H_6$.

Again the reaction might be still more complete giving carbon dioxide, the methyl and ethyl groups, or perhaps carbon dioxide and propane, and possibly some ethane and butane. These should yield methane, ethane and carbon dioxide, if hydrogen is present at the time of decomposition:

(3) $CH_3COOC_2H_5 \longrightarrow CO_2+C_3H_8$, and with hydrogen
$CH_3COOC_2H_5+H_2 \longrightarrow CO_2+CH_4+C_2H_6$.

Finally, two molecules of the ester might break up simultaneously to give carbon dioxide, ether and acetone, thus:

(4) $2CH_3COOC_2H_5 \longrightarrow CH_3COCH_3+(C_2H_5)_2O+CO_2$.

The acetone could then decompose to give methane, carbon monoxide, hydrogen, carbon and small amounts of ethylene and ethane. It should be noted that when two dissimilar radicles are formed in the decomposition these may combine with each other or with themselves to form higher hydrocarbons of various types.

Therefore, a study of the products formed when the ester alone, or the ester mixed with hydrogen, is passed over nickel should throw some light on the mechanism of the decomposition. Briefly summarized, if the ester decomposes according to (1), the addition of hydrogen to the vapor before passing over the nickel should form methane and ethyl formate, or its decomposition products. If it should break up according to (2), the hydrogen should cause the formation of ethane and acetic acid. If (3) is the proper scheme, the ester alone should give propane and carbon dioxide; with hydrogen the products should be methane, ethane and carbon dioxide, or its reduction products. While according to (4) the ester alone should yield carbon monoxide, hydrogen, methane, carbon, carbon dioxide, or its reduction products, and small amounts of ethane and ethylene. Since hydrogen is already present in these decomposition products, the addition of more hydrogen should not greatly alter them.

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[1] Mond, Langer and Quincke: Chem. News, 62, 95 (1890).
[2] Sabatier and Senderens: Bull., (3) 29, 295 (1903).

The temperature at which a catalytic reaction takes place greatly affects the reaction products, therefore, we should expect the decomposition products of ethyl acetate to vary with the temperature. Since the activity of a catalyst is affected by its age, due to change of form, or to accumulation of poisons, or to both, we might expect these decomposition products to change considerably with continued use of the same sample of catalyst, even under the same conditions. The purpose of the present investigation was to study the products formed when ethyl acetate is decomposed by nickel at various temperatures, and to determine the influence of added hydrogen upon these products. By this means we hoped to determine more specifically the mechanism of the catalytic decomposition of ethyl acetate by nickel.

Materials

The ethyl acetate was purified according to the method used by Wade and Merriam[1]. The crude ester was distilled three times from a large quantity of water and dried with anhydrous potassium carbonate. Two grams of water were added to each 500 cc. of ester and one-fifth of the mixture was distilled through a twenty inch evaporating column. The remainder was distilled four times from a large quantity of water, dried over anhydrous potassium carbonate for two days, then over phosphorus pentoxide, and finally fractionated. Its density was found to be 0.8879 at 30°; this value agrees closely with the value 0.8880 reported by Wade and Merriam.

Ordinary "C.P" nickel nitrate was twice recrystallized from a dilute nitric acid solution. The crystals were heated in an open evaporating dish below red heat until the evolution of the oxides of nitrogen ceased. The resulting nickel oxide was pulverized and stored in a desiccator. When needed a column of the oxide about 30 cm. long was loosely packed into a 5 mm. pyrex tube and held in place by two wads of glass wool. The oxide was reduced at the temperature at which the catalyst was to be used; this required about two hours. When first reduced the nickel is black in color, but after use for some time it became grey or brown, and was then only slowly soluble in dilute hydrochloric acid.

Apparatus

The hydrogen was produced electrolytically from a battery of generators containing a concentrated solution of sodium hydroxide. It was then completely dried by passing through a long tube of fused calcium chloride, two wash bottles containing concentrated sulphuric acid and two towers filled with solid sodium hydroxide; it was finally passed through a tube filled with copper gauze, heated to dull redness, to remove traces of oxygen.

The catalyst tube was heated in an electric tube furnace, the temperature of which was carefully regulated to within ±2.0° by a suitable external resistance. The temperature of the catalyst tube was determined by means of a delicate thermocouple fastened to the outside of the catalyst tube at the

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[1] Wade and Merriam: J. Chem. Soc., **101**, 2459 (1912).

center of the furnace. The ethyl acetate was introduced through a fine capillary tube which terminated close to the front end of the catalyst material; its vapor was carried through by the incoming hydrogen gas.

The products of the reaction were analyzed by means of the standard Burrell gas analysis apparatus. The absorption solutions were prepared exactly as specified by Purdy and Krauskopf.[1] An auxilliary 15 cm. pyrex tube of loosely packed copper oxide was also used for the fractional combustion of hydrogen and the hydrocarbons. It was covered with an asbestos shield and heated by a gas burner according to the method of White.[2] The 100 cc. water jacketed burette was provided with a manometer and a compensating tube to avoid the necessity of correcting for changes of temperature and pressure during an analysis. All barometer readings were made on a standard mercury barometer and were corrected for temperature, elevation and latitude.

Manipulation of Apparatus

The tube of nickel oxide was placed in the furnace and allowed to come to the desired temperature. Hydrogen was then admitted until the formation of water vapor ceased. The ethyl acetate was allowed to drop slowly in front of the catalyst, the heat at this point being sufficient to vaporize it and drive it through the catalyst. The products were led through a tube cooled with ice where the liquid portion condensed. Two samples of the gaseous portion were taken. One was collected in the burette and was analyzed for carbon dioxide and ethyl acetate; the other sample was collected in a bell jar over a solution of sodium hydroxide and was analyzed for carbon monoxide, hydrogen and the hydrocarbons. As soon as these samples were collected the ethyl acetate was shut off and the apparatus was washed out with hydrogen. The ethyl acetate was again admitted and two samples of the decomposition products from the mixture of ester and hydrogen were collected and analyzed as before. The resulting reaction products were studied at 300°, 350°, 400° and 450°; the measurements at each temperature were always repeated with new samples of the catalyst. A second run was made with the same sample of the catalyst at 400° in order to determine the effect of age of catalyst on the decomposition products.

Analysis of Products

The liquid product which was condensed in the tube at 0° was analyzed in two ways. Several samples were fractionated through a ten-inch distilling column and in no case did the corrected boiling point differ by more than 0.2° from that of the original ester. Several samples at each temperature were quickly titrated at 0° with N/20 sodium hydroxide and these showed no appreciable quantity of free acid. The samples of gas collected in the burette were analyzed for carbon dioxide and ester by allowing them to stand over the concentrated potassium hydroxide solution until there was no further

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[1] Krauskopf and Purdy: J. Ind. and Eng. Chem., 12, 158 (1920).

[2] White: "Technical Gas and Fuel Analysis," p. 54 (1913).

decrease in volume. Since the gas was saturated with the ester at the temperature of the ice bath the fraction by volume of the ester present was equal to the ratio of the vapor pressure at 0° to the barometric pressure at the time the sample was collected. This fraction of the loss over potassium hydroxide was considered ethyl acetate; the remainder of the loss in volume represents the volume of carbon dioxide present in the effluent products. The unsaturated hydrocarbons were removed from the samples collected in the bell jar over sodium hydroxide by means of fuming sulphuric acid. When these had been removed the remainder of the sample was passed over copper oxide at 240°, at which temperature the hydrogen and carbon monoxide are burned. The contraction following this combustion is equivalent to the volume of the hydrogen, since the change in the volume of the copper oxide and the volume of the liquid water formed are negligible; the contraction accompanying the subsequent passage of the residue over potassium hydroxide is taken as equal to the volume of the carbon monoxide. The remaining gases were again passed over copper oxide heated to 300°. At this temperature propane is burned and one half of the increase in volume following the combustion would be due to the propane. To determine the ethane present the residual gases are next passed over the oxide at 380°; the increase in volume following this combustion is equal to the volume of the ethane originally there. The remainder of the gas was considered as methane which burns over copper oxide only when heated to dull redness.

The experimental results obtained in this investigation are recorded in Tables I, II and III. Each value given is the means of at least two independently determined values. In Tables I and II the temperatures are given in the top horizontal row; the vertical columns contain the percentages of the constituents indicated at the left.

TABLE I

The Catalytic Decomposition of Ethyl Acetate alone by Nickel

	300°	350°	400°	450°
Ester	3.9	3.2	3.2	3.2
CO_2	9.5	8.95	17.4	18.8
H_2	32.15	33.55	18.2	13.8
CO	21.95	23.25	19.15	17.6
C_3H_8	00.00	00.00	00.00	00.00
C_2H_6	2.9	trace	00.00	1.05
CH_4	29.15	31.4	42.4	45.2
Unsat'd	0.6	trace	00.00	00.00
Acid	00.00	00.00	00.00	00.00
Total	100.15	100.35	100.35	99.65

A study of this Table shows certain conclusive facts. No decomposition of the ester as manifested by the evolution of gaseous products was observed at or below 280°. At 300° the evolution of gas is very slow, indicating that the ester begins to decompose not far below this temperature. There is no free acid obtained at any temperature; the same is equally true for propane. Except at the lowest temperature there is no appreciable quantity of unsaturated hydrocarbons. Ethane appears in a small quantity at 300°, but disappears at higher temperature only to reappear at 450°. At all temperatures some ethyl acetate was found to pass through the catalyst undecomposed.

As is evidenced from the Table the dominant reactions at the lower temperatures are those which lead to the formation of carbon monoxide, hydrogen and methane. From 350° to 450° the amounts of carbon dioxide and methane in the products show marked increase with increase in temperature; on the other hand, the percentages of carbon monoxide and hydrogen decrease, the decrease being especially marked with respect to hydrogen.

TABLE II

The Catalytic Decomposition of Ethyl Acetate by Nickel in the Presence of Added Hydrogen

	300°	350°	400°	450°
Ester	3.9	3.2	3.2	3.2
CO_2	0.5	0.00	8.6	15.05
H_2	90.3	82.15	53.2	12.60
CO	0.9	0.8	9.15	11.10
C_3H_8	0.00	0.00	0.00	0.00
C_2H_6	0.00	0.00	0.00	trace
CH_4	4.4	13.7	25.80	58.42
Unsat'd	0.00	0.00	0.00	0.00
Acid	0.00	0.00	0.00	0.00
Total	100.00	99.85	99.95	100.37

From Table II we see that there is no propane, free acid or unsaturated hydrocarbons formed at any temperature. The ethane appears only to a small extent at 450°, and some ester passes through undecomposed at all temperatures. The carbon dioxide and carbon monoxide are present in very small amounts at the low temperatures, but both increase with rise in temperature; this increase is even more marked in the case of methane. The amount of hydrogen in the decomposition products decreases regularly as the temperature is raised.

As previously stated ethyl acetate may decompose in four possible ways. Let us consider each of these in turn to see which of them agree with the observed facts.

I. According to the first possibility the ester molecule may decompose thus: $CH_3COOC_2H_5 \longrightarrow CH_3- + -COOC_2H_5$.
If these groups recombined or rearranged further ethane might be formed by the combination of two methyl groups; we might obtain carbon dioxide and propane from the combination of the methyl and ethyl groups; two complex $-COOC_2H_5$ groups might decompose to give two ethyl groups, combining to form butane, and two molecules of carbon dioxide, or they might decompose in a slightly different way to form carbon monoxide, carbon dioxide and ether. While no data were found relative to the catalytic decomposition of ether by nickel it might be safe to assume that possibly through dehydration and the intermediate formation of ethylene, ether is decomposed to form methane, water and carbon:

$$(C_2H_5)_2O \longrightarrow H_2O+(2C_2H_4 \longrightarrow 2CH_4+2C).$$

In any case, according to this scheme, ethane or higher hydrocarbons should be produced in considerable quantities. But aside from a very small amount of ethane no higher hydrocarbons were detected in the gaseous products.

If hydrogen were added to the ester decomposing in this way, we should expect the possible formation of methane and ethyl formate:

$$CH_3- + -COOC_2H_5+H_2 \longrightarrow CH_4+HCOOC_2H_5.$$

Ethyl formate, according to Sabatier and Mailhe[6], decomposes to form carbon monoxide and ethyl alcohol: $HCOOC_2H_5 \longrightarrow CO+C_2H_5OH$. Sabatier and Senderens have shown that ethyl alcohol vapor over nickel at 230° decomposes to give acetaldehyde and hydrogen, and at 330° the acetaldehyde further decomposes to form carbon monoxide and methane:

$$C_2H_5OH \xrightarrow{230^\circ} H_2+(CH_3CHO \xrightarrow{330^\circ} CH_4+CO).$$

These facts indicate that the final decomposition products from ethyl acetate in the presence of hydrogen should be methane, carbon monoxide and hydrogen. According to Sabatier and Senderens[1], the carbon monoxide should decompose further to form some carbon dioxide and free carbon. These products were the ones actually found in the analysis. However, this scheme would demand a difference in the nature of the products when the ester is decomposed in the presence of hydrogen and when it is decomposed in the absence of added hydrogen. No difference other than in the relative quantities of the products was observed.

II. According to the second scheme the molecules of the ester should first split into the ethyl and acetate radicles: $CH_3COOC_2H_5 \longrightarrow CH_3COO- +C_2H_5-$. These probably would react to form butane, carbon dioxide and ethane; or carbon dioxide and propane; or perhaps carbon monoxide, carbon dioxide and ether. The addition of hydrogen should cause the formation of acetic acid and ethane: $CH_3COO- + -C_2H_5+H_2 \longrightarrow CH_3COOH+C_2P_6$. This mode of decomposition either with or without hydrogen requires the

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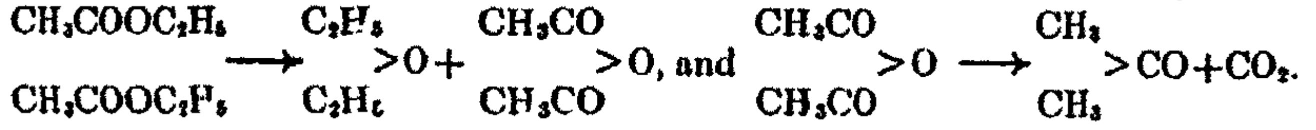
[1] Bull. (3) 29, 295 (1903).

formation of ethane and the higher hydrocarbons: the small amounts of these actually obtained show conclusively that this is not the mechanism of the reaction.

III. The third theoretical possibility presumes a decomposition of the ester into three parts: $CH_3COOC_2H_5 \longrightarrow CH_3- + CO_2 + C_2H_5-$. We might reasonably expect the methyl and ethyl groups to combine among themselves to form ethane and butane, respectively, or to combine with each other to form propane. If the decomposition takes place in the presence of hydrogen, the only products formed should be methane, ethane and carbon dioxide, or its reduction products, thus $CH_3- + CO_2 + C_2H_5 + H_2 \longrightarrow CH_4 + CO_2 + C_2H_6$. This third scheme does not account for the presence of hydrogen and carbon monoxide which are formed at all temperatures when the ester alone is decomposed in the presence of nickel. This together with the fact that no propane and only slight traces of ethane are ever found indicates that our third assumption does not represent the true course of the reaction.

IV. The fourth possibility permits two molecules of the ester to decompose simultaneously to give carbon dioxide, ether and acetone, thus:



$$\begin{array}{l}CH_3COOC_2H_5\\CH_3COOC_2H_5\end{array} \longrightarrow \begin{array}{l}C_2H_5\\C_2H_5\end{array}\!>O + \begin{array}{l}CH_3CO\\CH_3CO\end{array}\!>O, \text{ and } \begin{array}{l}CH_3CO\\CH_3CO\end{array}\!>O \longrightarrow \begin{array}{l}CH_3\\CH_3\end{array}\!>CO + CO_2.$$

The acetone decomposes further[3] to form hydrogen, carbon monoxide, methane, carbon and small quantities of ethane and ethylene:

$$CH_3COCH_3 \longrightarrow CH_4 + CO + H_2 + C + \ldots.$$

The ether might be expected to form methane, water and carbon, as shown in I.

The mode of decomposition postulated in IV requires the formation of carbon dioxide, carbon monoxide, methane, free carbon, and small amounts of ethane and ethylene. No ethylene was found, but, with the exception of traces of ethane at the lowest and highest temperatures, all of the remaining substances were actually found in the decomposition products. Since hydrogen is formed in the decomposition of the ester, the addition of more hydrogen should cause no great change in the products, except in the relative quantities. This was also found to be true.

The similarity of the decomposition products formed when ethyl acetate is decomposed by nickel, either with or without the presence of hydrogen, precludes the possibility of the decomposition having proceeded according to I. The absence of any considerable amount of ethane or higher hydrocarbons in the decomposition products disproves scheme II, while scheme III fails to account for the formation of carbon and carbon monoxide which are always found. The decomposition products required by scheme IV, however, agree with those found by experiment. The addition of hydrogen caused but little change in the decomposition products, which is also in agreement with the theory. Furthermore, this mode of decomposition is similar to that given by Sabatier and Mailhe for the decomposition of acetic acid. Therefore, we believe that this scheme represents most accurately the mechanism of the catalytic decomposition of ethyl acetate by nickel.

In Table III are given the results of the analyses of the decomposition products obtained by passing the ester over nickel that had been previously used. This experiment was undertaken because it was observed early in the work that the analyses of the decomposition products obtained in passing the vapor over the nickel varied considerably with the age of the catalyst. The analyses were easily duplicated, however, when fresh samples of the same or different catalyst were used. The sample of catalyst had been used for approximately four hours at 400°. It was then heated in a stream of pure dry hydrogen for several hours at that temperature; ethyl acetate was again passed over the nickel and new samples of the decomposition products were collected and analyzed. The columns (I) represent the mean of two values at 400° as given in Tables I and II for new samples of the catalyst. Columns (II) contain the values found by the analysis of the decomposition products over the previously used nickel.

TABLE III

The Influence of Age of Catalyst upon the Decomposition of Ethyl Acetate at 400°

	Ester alone		Ester+Hydrogen	
	I.	II.	I.	II.
Ester	3.2	3.2	3.2	3.2
CO_2	17.4	8.2	8.6	6.3
H_2	18.2	21.9	53.2	60.9
CO	19.1	27.9	9.1	11.0
C_3H_8	00.0	00.0	00.0	00.0
C_2H_6	00.0	00.0	00.0	00.0
CH_4	42.4	38.7	25.8	18.6
Unsat'd	00.0	00.0	00.0	00.0
Acid	00.0	00.0	00.0	00.0
Total	100.3	99.9	99.9	100.0

From these data it is obvious that the catalytic properties of nickel toward ethyl acetate are changed by continued use. With this change in properties there is a change in the trend of the reaction, but not in the nature of the products. Whether we use the ester alone or a mixture of the ester and hydrogen, the percentages of the carbon dioxide and methane in the products are decreased, while those of carbon monoxide and hydrogen are increased. Two reasons may be advanced for this change in activity. First, the quantity of carbon monoxide in the effluent products is considerable, and carbon monoxide has been repeatedly shown to be a powerful poison for nickel in catalytic reactions. Second, other decomposition products may alter the surface of the catalyst. Scheme IV which seems to most nearly represent the mechanism of ester decomposition involves the deposition of some carbon. Further, freshly reduced nickel dissolves rather rapidly in hydrochloric acid; samples of the nickel which had been used dissolve exceedingly slowly in the same acid. This would confirm the belief that the surface of the nickel becomes coated with some product that decreases its activity. In corroberation it may be stated that not only does the color of the nickel change, but there is deposited on the tube at each end of the catalyst column a dark brown film of unknown composition.

Summary

1. The products of the catalytic decomposition of ethyl acetate by nickel have been studied at 300°, 350°, 400° and 450°.

2. The temperature at which ethyl acetate begins to decompose has been found to be slightly below 300°.

3. The proportions of carbon dioxide and methane in the decomposition products were found to increase with rise in temperature; those of hydrogen and carbon monoxide decrease under the same conditions. Traces of ethane appear only at 300° and 450°. No higher hydrocarbons or free acid were found at any temperature.

4. The addition of hydrogen to ethyl acetate vapor before passing over finely divided nickel produces little change in the nature of the decomposition products, indicating that the mechanism of the decomposition is the same with or without hydrogen.

5. The activity of the catalyst is altered by some of the products of the decomposition of the ester.

6. A scheme representing the catalytic decomposition of ethyl acetate by nickel has been suggested.

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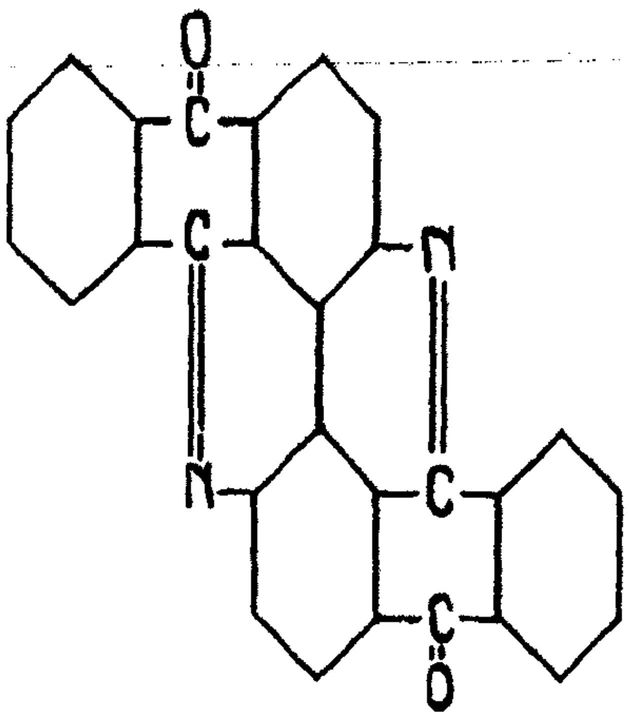
THE REDUCTION OF CERTAIN VAT DYES BY MEANS OF ALKALINE SODIUM HYDROSULFITE[1, 2]

BY JOHN H. YOE

I. Introduction

Recently[3] a study has been made of the action of alkaline sodium hydrosulfite on an oxyindanthrene dye (orange) of the formula



The results of this investigation indicated that the reaction between the dye and the alkaline hydrosulfite is very rapid, that an insoluble crystalline reduced dye (dark blue) is first formed, and that the latter is then peptized by hydroxyl ions to form a dark blue sol. The *rate* of peptization, and the *amount* of *dye stuff* peptized by a given solution, depend upon the state of sub-division of the dye. The rate of reduction is much faster than the rate of peptization. The sol is coagulated by positive ions. The present paper represents the results of a continued study of the action of alkaline sodium hydrosulfite on various vat dyes of the following formulas:

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[1] Contribution from the Cobb Chemical Laboratory of the University of Virginia.

[2] Published by permission of Dr. C. M. Stine, Chemical Director of E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware.

[3] Yoe and Edgar: J. Phys. Chem. 27, 65 (1923).

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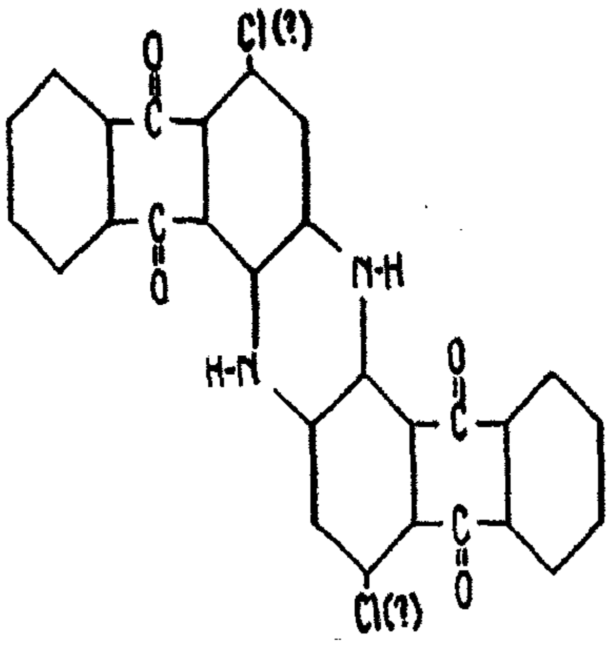
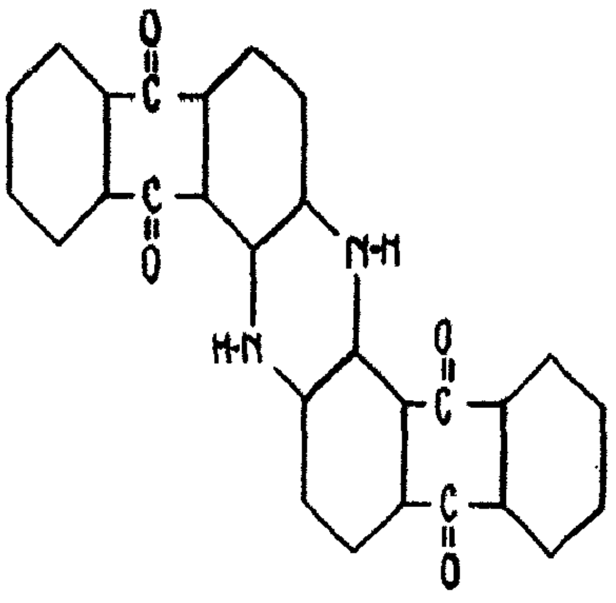
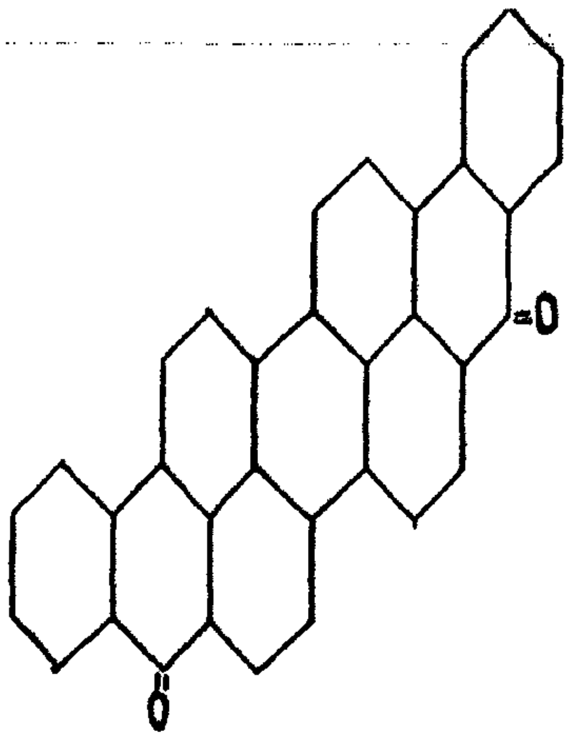


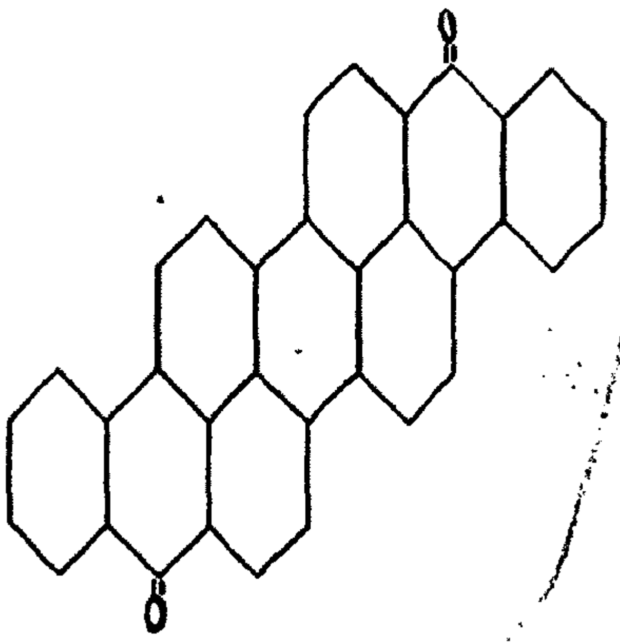
PONSOL BLUE G



PONSOL BLUE R



PONSOL DARK BLUE BR



PONSOL VIOLET RR

The dyes were furnished by the du Pont Company and were of high purity.

II. Experimental

In order to gain some idea of the rates of reduction of the different dyes at room temperature (21.5°C.) the following experiment was made: 0.05 gram of each dye was put in separate beakers containing 6cc. of 6-N NaOH and 50cc. of water. After getting the dyes in suspension, 1.5 g. of $Na_2S_2O_4$ was added to each mixture and the time noted. The mixtures were frequently stirred. The time to the first appearance of color in each mixture was recorded and times to successively darker shades were taken. The results are given in the following table.

TABLE I

Ponsol Blue G	Ponsol Blue R	Ponsol Dark Blue BR	Ponsol Violet RR
1 min. 40 sec.	4 min.	11 min.	8 min.
Pale greenish-blue	Pale blue	Pale bluish-gray	Pale bluish-gray
2 min. 45 sec.		27 min.	
Pale blue		Pale violet	Pale blue
15 min.		35 min.	35 min.
Fairly dark blue		Violet	Fairly dark blue

Taking the time to the initial appearance of color as a measure of the rate of reduction, it will be noted from the results above that the Blue G dye is much more rapidly reduced (at room temperature) than the other dyes. The particles of Blue G are spherical and 2 to 3μ in diameter. The Blue R particles are needle-shaped crystals, 10-20μ long and 2 to 5μ in width. Apparently many of the particles are crystal fragments. Dark Blue BR and Violet RR consist of spherical particles, for the most part 5 to 20μ in diameter, although some of the particles are only 2 or 3μ in diameter. Since the particles of Blue G are the smallest, other things being equal, the rate of reduction should be the greatest. However, even with the dye (Blue G) in the finest state of division the rate of reduction (or peptization of the reduced product) is extremely slow compared with Ponsol Yellow G, the dye stuff employed in the experiments of Yoe and Edgar[1]. Under similar conditions as those in the above experiments (Table I), this Ponsol Yellow G gives a blue color in 2 or 3 seconds and a dark blue in 20 seconds. At the end of one minute the solution is an intense cobalt blue. Moreover, Ponsol Yellow G crystals offer very much less surface than any of the other dye stuffs. It consists of long needle-shaped crystals, 50 to 300μ in length and 5 to 15μ in diameter. Even when compressed into a tablet (9.5 mm. diameter), this dye shows a rapid rate of reduction and solution (peptization).

In order to have a measurable and uniform surface, Ponsol Blue G was compressed into a tablet (9.5 cm. diameter) by means of a steel cylinder and plunger just as had been done in the case of Ponsol Yellow G. The dye tablet was then put in a flat steel holder and adjusted so that its upper surface protruded about 0.5 mm. The tablet holder was then placed in the reduction vessel contained in a constant temperature bath. A screw-like stirrer was adjusted in the center of the vessel and 1 cm. from the bottom. The dye tablet was halfway between the center and the side of the vessal. During a run the speed of the stirrer was kept at 500 r.p.m. All reductions were carried out in an atmosphere of hydrogen. For details of the procedure and diagram of the apparatus see Journal of Physical Chemistry, 27, 65 (1923.)

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[1] J. Phys. Chem. 27, 65 (1923).

The rate of reduction (peptization) was followed by pipetting out a 10cc. sample at frequent intervals, diluting to 100cc., and matching the color with that of a previously standardized blue glass of uniform thickness. A Kennicott-Campbell-Hurley colorimeter was used.

Several runs were made with Ponsol Blue G at 25°C.±0.02°, and in sodium hydroxide solution 0.10 N, 0.50 N, and 1.00 N, respectively. In each case the amount of dye in "solution" at the end of the run (1 to 4 hours) was so small that the vat solution was almost colorless. At the end of the run the dye tablet was examined and found to be covered with a thin layer of the dark blue reduced dye.

Another run was made similar to those above (0.20 N NaOH) but at 40°C.±0.02°. The run was discontinued at the end of 5 hours. The vat solution was almost colorless but contained a flocculent, light blue precipitate.

Since the rate of reduction and solution (peptization) of the dye in tablet form is so slow (even at 40°C.) it was decided to use the original dye crystals. Preliminary tests having shown that peptization of the reduced dye is slow at 21.5°C. (see Table I.)., the temperature was kept at 40°C. In each run 0.100 g. of Ponsol Blue G crystals was put in the reduction vessel and 500cc. of sodium hydroxide (of known strength) were added. After the temperature became constant, the $Na_2S_2O_4$ was added. In one series of runs the concentration of the sodium hydroxide was varied, the amount of $Na_2S_2O_4$ being kept constant at 5 grams; in a second series the sodium hydroxide was kept constant at 0.25 N, and the amount of $Na_2S_2O_4$ varied.

The data are recorded in the following tables and represented graphically in Figs. 1, 2 and 3. Curve II in Fig. 1 was obtained by taking the average data of two runs with 0.10 N, NaOH (Table II).

TABLE II

Reduced Dye in Solution (mgs. per liter).

Tem. = 40°C.; Stirrer = 500 r.p.m.; 5 g. $Na_2S_2O_4$.

Conc. NaOH	0.05 N	0.10 N	0.10 N	0.25 N	0.50 N	1.00 N
Time (min.).	Concentration of Reduced Dye (mgs. per liter).					
5	47	156	153	229	151	91
10	76	204	185	244	197	122
15	97	228	206	248	207	132
20	110	241	220	248	206	132
25	120	248	228		202	132
30	125	248	232			
35		248	234			
40		248				

TABLE III

Reduced Dye in Solution (mgs. per liter).
Temp. = 40°C.; Stirrer = 500 r.p.m.; 0.25 N NaOH.

Weight $Na_2S_2O_4$	1 G.	5 G.	10 G.	20 G.
Time (min.).	Concentration of Reduced Dye (mgs. per liter).			
5	205	229	235	240
10	205	244	248	252
15	197	248	252	255
20	193	248	252	256
25			252	257
30			252	258

III. Discussion of the Data

(a) General Nature of the Reaction Velocity Curves.

The curves in Figures 1 and 3 show that the initial rate of reduction and solution is very rapid, most of the solution taking place within the first five minutes. The rate then slows up and becomes practically constant in 20 to 30 minutes or in some cases may even pass through a maximum due to a partical agglomeration of the reduced dye particles (see curve IV in Fig. 1). The general shape of the curve is the same as that obtained with Ponsol Yellow G previously reported[1].

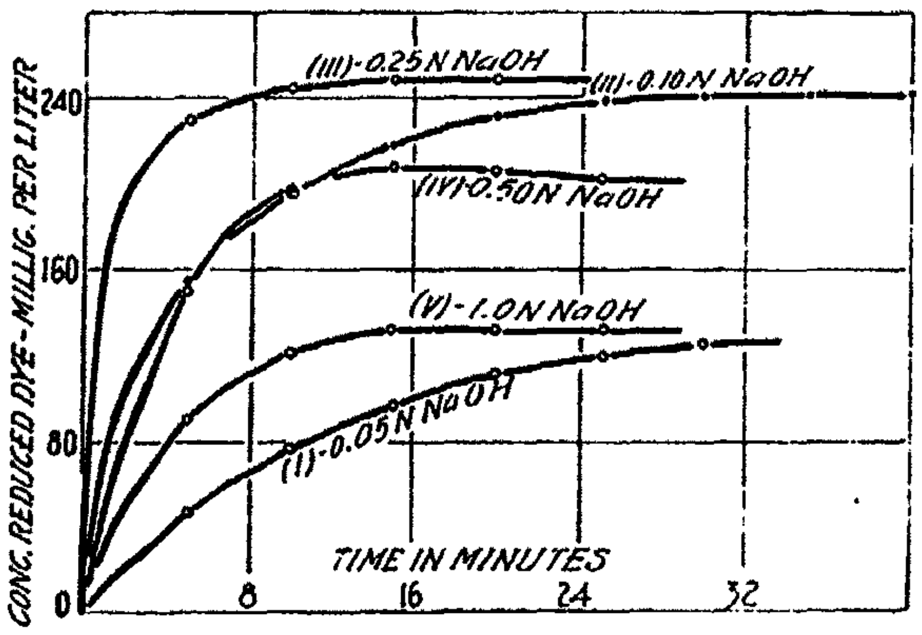

FIG. 1
Effect of Alkali Ion

(b) Effect of $Na_2S_2O_4$.

Examination of the curves in Fig. 2 shows that the concentration of the $Na_2S_2O_4$ has very little effect upon the reduction and solution of the dye,

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[1] Yoe and Edgar: J. Phys. Chem. 27, 65 (1923).

provided a sufficient amount is present. With 5, 10 and 20 grams of the hydrosulfite, the concentrations of reduced dye at the end of 10 minutes were 244, 248, and 252 mgs. per liter, respectively. This result is in agreement with that obtained in the case of Ponsol Yellow G. previously reported.

(c) Effect of Sodium Hydroxide.

As seen in Fig. 1, sodium hydroxide has a marked effect upon the reduction and solution of Ponsol Blue G. The effect is seen to pass through a maximum at a hydroxide concentration of about 0.25 N. This is brought out more strikingly in Fig. 2 in which the concentration of reduced dye is plotted against the normality of sodium hydroxide at constant time intervals. Here again, the result is in agreement with that obtained with Ponsol Yellow G, i.e., for a given set of conditions, there is an optimum sodium hydroxide concentration. A quantitative comparison with the results obtained with Ponsol Yellow G, however, is not possible because in the latter experiments the temperature was 25°C. and the dye stuff in the form of a tablet.

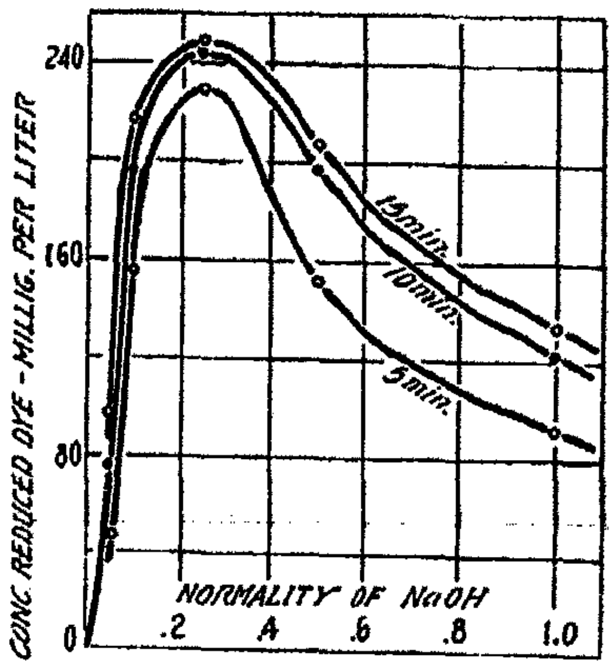

Fig. 2
Effect of Alkali Ion. Conc. Dye vs. Normality of NaOH at Constant Time.

In addition to the experiments recorded in Table II, several runs were made in which the NaOH concentration was 0.01 N and 3.00 N, respectively.

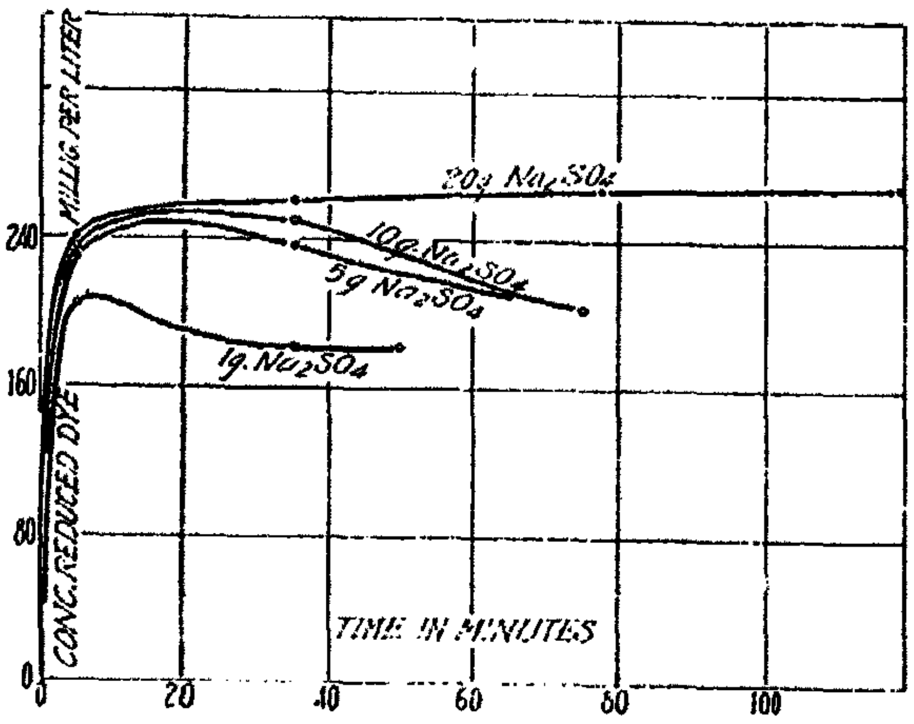

Fig. 3
Effect of Sodium Hydrosulfite

In each case the amount of reduced dye (even after two hours run) was so small as to preclude measurement. The vat solution had a pale blue color.

The results given in Table II indicate that hydroxyl ion favors the rate of solution (peptization) while sodium ion retards it. A further indication of this was obtained by carrying out an experiment in a solution 0.25 normal in NaOH and 0.25 normal in NaCl. The rate of solution was much slower than when 0.25 N NaOH alone was used, a result in accord with that obtained with Ponsol Yellow G.

(d) Indications of the Colloidal Condition of the Reduced Dyes.

The above experiments indicate that the reduced dye is probably in colloidal suspension instead of in true solution, and that we are accordingly dealing with a peptization phenomenon. Further evidence of the colloidal nature of the Ponsol Blue G solutions and also solutions of Ponsol Blue R, Ponsol Dark Blue BR, and Ponsol Violet RR is obtained from the fact that upon filtering the alkaline reduced solutions through hardened filter paper, the filtrates are water-clear and colorless, while in each case a layer of reduced dye is found adhering to the filter paper. Moreover, solutions of all of the reduced dyes are readily coagulated by inorganic salts.

IV. Summary

1. Measurements have been made of the rate of reduction of centain vat dyes by alkaline sodium hydrosulfite solutions.

2. The effect of temperature, sodium hydroxide, sodium hydrosulfite, and electrolytes has been observed for a given set of conditions.

3. The rate of reduction is very rapid but that of "solution" of the reduced product is much slower.

4. It seems that the reduced product is in colloidal suspension and not in true solution. Hydroxyl ion seems to peptize the reduced dye but this action may be more than off-set by a high concentration of a metal ion.

5. Inorganic salts cause agglomeration of the reduced dye.

6. All results are in good agreement with those previously obtained in this laboratory with a similar dye.

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THE ACTION OF CHLORINE ON MERCURY

BY ALBERT F. O. GERMANN

In an article on "Active Chlorine", by Y. Venkataramaiah,[1] published recently in this Journal, an apparatus is described for the measurement of the volume change occurring in a given mass of chlorine at constant temperature under the influence of the silent electric discharge. The volume change was observed on a mercury manometer, communicating with the main body of the apparatus through a capillary tube of one half millemeter bore. It is not clear from the description whether chlorine actually came in contact with the mercury, or whether this portion of the apparatus contained air, but one is inclined to believe, from the context, that chlorine and mercury were left in contact for the duration of the experiment, ten hours. The author says:—

"The manometer contained pure dry mercury. It was shown by Shenstone that pure dry chlorine has no action on pure dry mercury. In the present arrangement there is little chance for the active gas to come in contact with the dry mercury through the capillary tube."

Mr. Venkataramaiah tacitly agrees with the statement credited to Shenstone, and one would be justified in the conclusion that he found pure dry chlorine inert towards pure dry mercury.

Without wishing to belittle the importance of the work on active chlorine, my impression is that this would be far overshadowed by the feat of producing inactive chlorine. But I am frankly skeptical, and look forward to a positive statement regarding the matter with much interest.

As a matter of fact, Shenstone, after performing elaborate experiments on this subject[2] came to the reluctant conclusion that "the action between mercury and chlorine, bromine, or iodine does not depend on the presence of water vapour." That he had not revised this opinion at the time of his death, is attested by his friend, Sir W. A. Tilden, whose assistant Shenstone was at Clifton College, and whose successor he became when Dr. Tilden was called to Mason College. In an obituary notice Dr. Tilden[3] said:—"The results of these experiments led him to the conclusion that chlorine, bromine and iodine when in the highest known condition of purity, dried by contact under special conditions with phosphoric oxide for six months or more, do at once combine with mercury when brought into contact with that metal similarly purified and dried."

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[1] Y. Venkataramaiah: J. Phys. Chem., 27, 79 (1923).

[2] W. A. Shenstone: J. Chem. Soc., 71, 479 (1897).

[3] W. A. Tilden: J. Chem. Soc., 95, 22 6 (19 9).

Similar evidence is given by Cowper,[1] who found that chlorine which was inactive towards sodium even when melted, readily attacked mercury, tin, antimony and arsenic.

One is inclined to attribute the action of chlorine on arsenic, antimony and tin to the formation of liquid chlorides, and its action on mercury to the fact that mercury differs from other metals yielding solid chlorides in its liquid state, and the readiness with which a new surface is presented for reaction with the gas. But then melted sodium ought also to be attacked, and Cowper says that after some initial action, which he attributes to imperfect drying, melted sodium remains untarnished in an atmosphere of chlorine gas. A similar observation was made by Wanklyn some years before.[2]

While my own experiments on this subject are by no means as rigorous as those cited above, they still have some interest. I have had frequent occasion to prepare pure dry chlorine. On these occasions my secret conviction that really pure chlorine would not attack mercury always prompted me to use every precaution in the purification, and to try the experiment; but the results have been uniform—combination proceeds with undiminished vigor.

It is known that phosgene does not attack metals, except at an elevated temperature, when it is probably chlorine resulting from dissociation that is responsible for the action. Phosgene hydrolyzes in the presence of moisture, producing hydrogen chloride and carbon dioxide; while this reaction has not been shown to be reversible, it is known that concentrated hydrochloric acid retards the hydrolysis.[3] Hence larger amounts of water are only slowly destroyed by phosgene. But small amounts of water should be rapidly decomposed by phosgene, especially at an elevated temperature. In an effort to dry my materials with phosgene, I partially filled a tube with liquid phosgene and left it for some time at room temperature. I then allowed the phosgene to boil away, and heated the tube with the free flame, evacuating the while; after several repetitions of this process, I distilled several grams of pure mercury into the tube from a side tube, which had also been subject to the phosgene and heat treatment. Several days before I had prepared in another tube a solution of pure chlorine in liquid phosgene, and kept it at room temperature, in the hope that any traces of moisture might be destroyed. This solution was finally distilled in to the tube containing the mercury, which immediately reacted completely with the chlorine.

In this experiment it is of course possible that phosgene played the usual role of water, and that the reaction was catalyzed by phosgene. But this is extremely improbable, as Klein has shown[4] that in the reaction between hydrogen sulfide and sulfur dioxide, which takes place in the presence of a trace of water, the reaction is also induced by fifteen substances, including alcohols, ketones, nitriles, esters, ether and carvone, but not by carbon disulfide, ethyl

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[1] Richard Cowper: J. Chem. Soc., 43, 153 (1883).

[2] J. A. Wanklyn: Chem. News, 20, 271 (1869).

[3] See Delépine, Douris and Ville: Bull. 27, 286 (1920).

[4] David Klein: J. Phys. Chem., 15, 1 (1911).

disulfide, benzol, amylene, chloroform, carbon tetrachloride, ethyl chloride, acetyl chloride, benzoyl chloride and nitrobenzene. Of the five halogen derivatives tested, not one was able to catalyze the reaction studied. This evidence is substantiated by the observation that chlorine dissolved in liquid phosgene does not attack magnesium. The fact that chlorine dissolved in phosgene attacks aluminium[1] has no bearing on this point, because aluminium chloride is soluble in phosgene. In fact, it has been shown[2] that phosgene itself reacts with metals in the presence of aluminium chloride, with which the metallic chloride produced in the reaction forms soluble complexes.

Conclusion. With the exception of the implied experience of Mr. Venkataramaiah, there seems to be no record of chlorine showing itself inert towards mercury. It would be very much worth while to have a detailed account of his research with particular reference to "inactive chlorine".

Addendum. The December number of this Journal (27, 951 1913) has an unindexed note containing corrections to Venkataramaiah's article, which the writer has since found. In this, besides numerical corrections which seem to diminish the certainty of some of the conclusions drawn by V., the statement is made that the manometer contained *fused silver chloride* instead of mercury. The writer refrains from making any comment upon this correction, and trusts the reader to draw his own conclusions.

A. F. O. G.

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California.

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[1] A. F. O. Germann: Science, 58, 309 (1923).

[2] A. F. O. Germann and K. Gagos: Science, 58, 309 (1923).

NEW BOOKS

Clouds and Smokes. *By William E. Gibbs with a foreword by Sir Oliver Lodge. 22 × 15 cm; pp. xiii + 240. Philadelphia: P. Blakiston's Son and Co., 1924. Price: $3.00.* In the foreword Sir Oliver Lodge says: "There is one part of the book in which I am sure to be specially interested, for I remember that it was in 1884 that I exhibited the effect of electrification in clearing a space of smoke, fume, or mist, a phenomenon which was afterwards found to have been casually observed and not developed by a Mr. Guitard so long ago as 1851, as recorded in the *English Mechanic* of that date. My sons, of the Lodge Fume Deposit Company, Great Charles Street, Birmingham, after long and continued trials, made the process really practicable, and have now combined with my friend Mr. F. G. Cottrell, who so successfully established it on a large scale in America. It is amazing to me to see the Lodge-Cottrell process at work continuously, night and day throughout the year, with a potential of hundreds of thousands of volts, giving a continuous current of sparks—or what Crookes more properly called a nitrogen flame—and, by the aid of great electrified chambers, clearing immense quantities of blast furnace gas of dust at Skinningrove, in Yorkshire, and elsewhere, and also depositing sublimated and previously wasted metallic ore, as, for instance, at the tin-smelting furnaces of Messrs. Williams, Harvey and Co., at Bootle, near Liverpool. The step from a laboratory experiment to a really practical and commercially continuous process is undoubtedly a great one, and the credit for it belongs to others than myself. It is, however, delightful to see the electrical process of clearing air gradually come into operation at manufacturies all over the world, and I see that the author of this book has given an indication of the kind of arrangement employed. Short of inspection of the working operation, however, no adequate idea can be gained of the remarkable character of this engineering achievement."

The chapters are entitled: introductory; the formation of aerosols; the movements of the particles; general properties of aerosols; the stability of aerosols; the chemical and physical examination of an aerosol; the industrial treatment of fumes and dusty gases; dust explosions; meteorology; the industrial preparation and utilisation of substances in a finely divided condition; smoke in warfare.

On p. 30 there is an account of the critical temperature of condensation of metallic vapors. "From a consideration of the behavior of various metal vapours Knudsen and Wood suggested that, when a metal molecule encounters a surface of the same metal, it always adheres to it, the intermolecular force of attraction being stronger than the force of rebound. When the metal molecule meets a surface of another material, however, it may adhere or rebound according to the temperature—*i.e.*, according to the velocity of rebound. For a given surface there will be a critical temperature of contact, above which the molecule will rebound, and below which it will adhere. For mercury molecules striking a glass wall the critical temperature is about −135°C. For silver molecules striking a glass wall it is about +575°C.

"At temperatures above this critical point it is possible to obtain very high degrees of supersaturation, since all the molecules are reflected. If, however, condensation be induced at any point of the surface—for example, by touching the wall of the containing vessel with a cotton plug dipped in liquid air—so that a metal surface is formed, then condensation continues upon this metal surface, even after it has warmed up again. Cadmium, magnesium and zinc show this phenomenon readily in glass vessels. According to Knudsen, the critical temperature for these metals lies below −78°C.

"Silver, gold, platinum, tungsten, molybdenum, nickel, iron, copper, do not behave in this way. When wires of these metals are heated electrically *in vacuo*, the metal molecules are sent out in straight lines and adhere to the glass wall of the containing vessel. Owing to the complete absence of reflection from the glass surface, any obstacle that is placed between the wire and the glass will cast a well-defined shadow within which no metal will reach the glass at all. Other metals, including cadmium, magnesium, zinc, behave similarly below the critical temperature."

"According to Ehrenhaft, particles of various substances of the order of magnitude of 10^{-4} and 10^{-6} cm., suspended in a gas, are attracted or repelled by the intense light of an electric arc. Spherules of gold, silver and mercury, produced in pure nitrogen, and particles of the smokes of turpentine and camphor, are repelled. Sulphur and selenium particles distilled in argon, droplets of nitric acid and its decomposition products in air, water mist, cigar smoke and wood smoke, are attracted. Fine droplets of water, suspended in oxygen or hydrogen, are not affected. The velocity of the displacement is increased by increasing the intensity of the light, or by diminishing the pressure of the gas.

"The existence of positive and negative photophoresis can be attributed to the same cause as that to which the action of the Crookes radiometer is due. Whether a particle will be attracted or repelled will depend upon its capacity for absorbing or transmitting radiant energy. In the case of a strongly absorbing particle, the illuminated side will be heated more than the other side; thus the impact between the gas molecules and the heated surface will be more vigorous than on the other side of the particle, so that the particle moves away from the source of light. Weakly absorbing particles—for example, sulphur and selenium—will permit the light to pass freely through them, so that the far side of the particle becomes warmed more than the illuminated side. Such particles, therefore, would move towards the source of light," p. 63.

On p. 65 we read that "Wood has shown that the cloud formed by the condensation of iodine vapour scatters deep red light, which is plane polarised in a plane parallel to the direction of the incident beam. The particles of this cloud were of an average diameter of 0.003 mm. By transmitted light the cloud appeared colourless. This abnormal polarisation is attributed to the transparency of the particles. A part of the incident beam will be reflected from the surface of the particles, will be colourless, and will be polarised quite normally in a plane perpendicular to the direction of the incident ray. The other part of the incident beam will be refracted and reflected inside the particles. It therefore undergoes absorption, and emerges highly coloured and polarised in a plane parallel to the direction of the incident ray. Similar behaviour was observed with a cloud of nitrosodimethylaniline."

"For most substances the intensity of the reflected light is almost independent of the wave-length. Some substances, however—for example, the metals and certain dyestuffs—show markedly selective reflection. They reflect waves of length approximately equal to those which they absorb. This selective reflection is attributed to the optical resonance of the particles at the surface of the substance. Optical resonance is a special case of fluorescence. If the resonating particles are separated by distances much larger than their diameters, as, for example, the particles of a cloud, the light may be absorbed and re-emitted on the further side from the source of light. Sodium vapour absorbs yellow light and transmits blue. Wood has shown, however, that the metallic fog produced by the condensation of sodium vapour scatters violet light, and transmits yellow. This appears to be due to the optical resonance of the metal cloud particles," p. 67.

"When a metal vapour is condensed, it is found that the coarsest condensates are formed in the entire absence of any indifferent gas. When such a gas is present—*e.g.*, nitrogen, carbon dioxide, hydrogen, bromine—then, according to the nature of the metal, finer condensates are obtained. The degree of dispersion is higher the greater the density and pressure of the gas. Thus finer condensates are obtained in nitrogen than in hydrogen, and at 760 mm. pressure than at 30 mm. pressure.

"In many—possibly in most—cases, the effect of adsorption is further complicated by the presence of gaseous ions in the dispersion medium. These will be adsorbed by the particles. They may be adsorbed indiscriminately, in which case they will impart charges of opposite sign to different particles, and thus promote flocculation. On the other hand, the particles may adsorb ions of one sign only, and thus, becoming charged with the same sign, exhibit no tendency towards flocculation.

"In some cases, the particles, either because of ion adsorption or because of their intrinsic structure and configuration, may be electrically polarised. Such particles will become attached to one another by their unlike poles, and thus tend to form peculiar thread-like aggregates.

"Whytlaw-Gray found that the particles of CdO and ZnO smokes form flexible string-like aggregates. The tendency to form such string-like complexes seems to be weakest with oxides of lead, manganese, copper, and chromium. It is slightly greater with iron, whilst magnesium, aluminum, and antimony, resemble zinc and easily form loose, flock-like aggregates.

"The particular structure of the aggregates that are formed by the particles of a given smoke appears to depend upon the nature of the substance of which the individual particles are composed rather than upon the influence of electrical charges on the particles. In the case of zinc oxide smokes, the formation of thread-like complexes, for instance, must be attributed to the intrinsically polar character of the particles themselves, since precisely similar complexes are formed in smoke that is formed by the decomposition of zinc ethyl in which very few charged particles are produced," p. 94.

"If a smoke is subjected to a high tension discharge, so that the molecules of the dispersion medium are charged, the particles of the disperse phase will become charged by ion adsorption. They will then be brought together by the force of the electric field, to form thread-like aggregates along the lines of force. These aggregates speedily settle to the floor of the container.

"The stability of a P_2O_5 or SO_3 smoke, when bubbled through water, is partly to be attributed to the presence of a film of adsorbed gas (air) surrounding the particles. The stability of the blue ZnO smoke from a brass foundry can be similarly explained. When the ZnO is collected—*e.g.*, with woollen filters—it is very light and mobile. It flows and surges in a bottle like a liquid, and has an apparent density of 0.1, the normal density of ZnO being 5.78. The ZnO smoke is rapidly flocculated by steam. Possibly the steam displaces adsorbed gas from the surface of the particles," p. 96.

"Ignition tests with an arc lamp, an oil lamp and a candle flame, carried out with various dusts, show a wide variation in the ease of ignition and the violence of the resulting explosion. A sample of rice dust that is easily exploded by a candle flame could not be ignited by an electric arc. A coal dust that ignited weakly with an arc exploded violently with a candle flame. Flour exploded readily with each source of ignition. Corn elevator dust that was not ignited by an arc or candle flame could burn round the flame of the oil lamp, but combustion was not propagated. In the classification on p. 166, the lowest temperatures are given at which various dust clouds will ignite when allowed to fall through a small porcelain tube heated to a definite temperature, and containing a roll of copper gauze. In this case, propagation is facilitated, since the whole of the cloud is heated. Higher ignition temperatures will be required to ignite such dusts at a single point.

"An explosion of a dust cloud can be restrained, or entirely prevented, by mixing with it a suitable proportion of inert dust, such as shale or limestone. Starch dust, for example, is easily exploded by a candle flame or arc, but a dust mixture of 30 per cent. starch and 70 per cent. shale cannot be ignited by either. Similarly, a mixture of 40 per cent. flour and 60 per cent. shale dust cannot be exploded by an arc. A dust cloud consisting of 40 per cent. sulphur and 60 per cent. shale can be exploded easily by a candle flame, but 30 per cent. sulphur mixed with 70 per cent. shale dust cannot. A mixture of 50 per cent. flour dust with 50 per cent. shale dust can be exploded by a candle flame, but is not ignited by an arc.

"Fine shale and limestone dust are used in coal mines to check the propagation of a coal dust explosion. The dust is contained on shelves or in boxes that are suspended from the roof of the mine galleries at various points, high enough to be clear of traffic. They are tripped by the advancing explosion wave, and discharge the dust into the air beneath, thus diluting the coal dust that is present in the air, and effectively checking further propagation of the explosion.

"The maximum velocity of flame propagation that has been observed during experiments with gas mixtures ranges from 5,000 feet per second for a mixture of carbon monoxide and oxygen to 9,000 feet per second for a mixture of hydrogen and oxygen. During experiments with coal dusts at different times, flame velocities of over 3,000 feet per second have been observed, while in certain tests there were indications that the velocity exceeded 6,000 feet per second. The flame velocity is increased by increasing the fineness of the dust, or by mixing a small amount of inflammable gas with the dust, and is higher and more dry the more free the dust is from ash and moisture," p. 174.

On p. 63 the author discusses the thermal precipitation of dust and on p. 202 he says: "Recently attempts have been made in America to dissipate clouds and fogs by sprinkling an electrically-charged dielectric—for example, sand—over the surface of the cloud from an aeroplane. In these experiments, a single aeroplane succeeded in dissipating a cloud a mile or two long and over one thousand feet deep, in a few minutes by using 100 lbs. of sand (150-mesh) charged to 14000 volts. It is possible that this method may be applied to the dissipation of the smoke fogs of the industrial areas."

Wilder D. Bancroft

Atomic Structure and Spectral Lines. *By Arnold Sommerfeld. Translated by Henry L. Brose from third German edition. 23 + 16 cm; pp. xiii + 626. New York: E. P. Dutton and Company, 1923. Price: $12.00.* In the preface the translator says that "since the appearance of the last German edition—on which this translation is modelled—new important facts have been discovered, tending to confirm ideas put forward here. Chief among these is the confirmation of the magnetic moment of the silver atom by Gerlach and Stern. It is strong evidence in favor of the theory concerning directional quantizing in the magnetic field, and opens up new regions of research which may lead to undreamed-of consequences. From their measurements Gerlach and Stern have deduced that, within the limits of error of their experiments, the magnetic moment of the normal silver atom in the gaseous state is one Bohr magneton. In a recent issue of the *Zeitschrift für Physik*, Einstein and Ehrenfest have discussed the important question as to how the magnetic atoms of silver can alter their directions at all under the influence of a magnetic field. Difficulties appear to arise akin to that of the 'time of accumulation' of energy quanta for Röntgen rays."

The subject is presented under the headings: introductory facts; the natural system of elements; Röntgen on X-ray spectra; hydrogen spectrum; wave theory and quantum theory; series spectra in general; band spectra; theory of the fine-structure; mathematical notes and addenda.

On p. 6 the author says: "The electron is a universal element of structure of all matter. Whether it is flowing along slowly in an electric current, or hastening through space at an extremely high rate as a cathode ray, whether it is emitted in radioactive disruption or in a photo-electric process, whether it is vibrating in our lamps (or, as we should now prefer to express it, 'jumping' in our lamps), whether it effects the course of light in telescopes, it is always the same physical unit, proving its identity by exhibiting the same charge and the same mass, in particular by keeping the ratio of charge to mass constant."

"The hardness of Röntgen light represents what we usually call colour in the case of ordinary light. Great hardness denotes great frequency of vibration or small wave-length. Moderate hardness or greater 'softness' denotes smaller frequency and greater wave-length. This terminology introduces no difficulty in the case of characteristic radiation. We called this free vibration and are tempted to ascribe to it a period (or a series of periods) of vibration characteristic of the material of the anti-cathode. This we may actually do, for experimental researches have fully confirmed this conclusion. The characteristic radiation is not only 'characteristic' but also 'homogeneous'. It consists of a few sharply defined kinds of vibration, each of which corresponds to a homogeneous monochromatic type of light. When we have become acquainted with the spectral resolution of X-rays, we shall see that the characteristic radiation assumes the form of a line spectrum," p. 28.

"As we saw, the hardness of the characteristic radiation depends on the atomic weight of the emissive material of the anti-cathode. On the other hand, the hardness of *impulse radiation depends essentially on the voltage of the X-ray bulb,* or on what is the same, the velocity of the impinging cathode rays; as is well known, the hardness increases with the voltage of the bulb. In the language of spectra this means that the *region of wave-lengths of greatest intensity in the continuous spectrum shifts towards the smaller wave-lengths as the voltage increases,*" p. 30.

"In the case of the photo-electric effect, too, we are dealing with the production of kinetic energy which is drawn from the energy supply of the incident radiation (the fraction that is absorbed). We should expect more intense light to produce a greater photo-electric effect, than less intense light. But this, as we saw, is not true. The power of the light is not determined by its *intensity* but by its *frequency.* Blue light has great power, red light but little. The intensity determines only the quantity but not the quality of the photo-electric action. These facts are very strange and depart greatly from the usual theoretical conceptions: they could not be explained on the basis of classical mechanics and optics. The key to them was furnished by the modern *theory of quanta,*" p. 36.

"There has been no dearth of attempts to reduce the contradiction between the "quantum" and the "classical" view of energy transference. In conjunction with Debye the author has put forward a view of photo-electric phenomena and a method of deriving Einstein's law, which does not deprive radiation of the character demanded of it by the wave theory, that is, which does not require the use of compact elements of energy of amount $h\nu$ and which, instead, ascribes to the atom the property of being able to pile up energy of radiation to a limiting amount determined by the constant h. As soon as this limit is reached the electron is supposed to be released from the atom and to escape with the energy which it has collected. Under certain conditions (chosen in rather an artificial manner) Einstein's law for the energy of the escaping electrons may be deduced. At the same time the 'time of accumulation' that is necessary for the heaping-up of the energy $h\nu$ may be calculated. If a powerful source of light is assumed, then this time in the case of the photo-electric effect comes out fairly small (fraction of a second), but when the calculation is made for the conditions of the X-ray photo-electric effect, for which the energy-element $h\nu$ is much greater and the intensity of radiation is, in general, much smaller, impossible 'accumulation times' come out, times of the order of magnitude of years! Yet experiment shows that, in the case of X-rays as well as in that of ordinary light, the emission of electrons commences immediately, as soon as the exposure to the incident light begins, and ceases the moment the exposure is stopped. From the point of view of the wave theory the source of the great energy of emission remains incomprehensible. The phenomena actually occurs as if in light of frequency ν there are ν energy-elements of the magnitude $h\nu$, which are ready at any moment to become transformed, according to Einstein's law (in atoms that are appropriate), into kinetic energy of electrons. Later, when we come to speak of the absorption and excitation of spectral lines, we shall find ourselves compelled to adopt this standpoint of light-quanta," p. 44.

"Both points of view, the classical continuous wave theory and the discontinuous-statistical theory of light-quanta, each offer at present only one-half the truth. How the dilemma will be overcome finally, cannot yet be gauged. At all events the classical wave theory in its application to the phenomena of light propagation has not yet been supplanted by something better. It is, indeed, astonishing how much of the wave theory still remains even in spectroscopic processes of a decidedly quantum character," p. 254.

"In conclusion we shall point out those features in which our treatment and the classical wave theory agree and those in which they differ.

"*They agree* in their views of the phenomena that occur in the ether. According to the wave theory, as well as ours, the ether vibrates, that is, it propagates alternating electromagnetic fields. We take over Maxwell's equations, which define the ether and regulate its vibrations, directly from the wave theory.

"*They differ* in their views of the excitation of the states of vibration. According to the wave theory, the electron that excites the ether also vibrates. It is forcibly coupled with the ether and impresses its time of vibration on the latter, which, according to the wave theory is prescribed by the nature of the bond between the electron and the atom. According to the view of the quantum theory, however, the coupling between the ether and the electron is less strong or more superficial. In its stationary orbits, the electron does not excite the ether at all, but is coupled to it only during the transition from one stationary orbit to another. The duration of vibration of the radiation has nothing to do with the revolution of the electron in its stationary paths. Even during the transition there is nothing in the atom that occurs in rhythm with the vibration number ν. The ether demands its $h\nu$, the atom furnishes it by giving up an amount of energy $W_a - W_e$. The duration of vibration follows if these two quantities are equated; at the same time, the polarisation follows if we equate the two corresponding moments of momentum. It has, indeed, been suggested that the transition from the stationary initial orbit to the stationary final orbit takes place along a spiral, which is traversed with the frequency ν. This too specialised picture seems to us unfruitful. *It is not the atom that vibrates, but the ether.* The coupling between the atom and the ether is, as we said, more provisional in the quantum theory than in the wave theory. The atom gives the ether a certain amount of energy and moment of momentum. The ether does with this, what its nature compels it to do, namely, it transforms these amounts into vibrations of a definite state of polarisation. The coupling is of an *integral* kind, not of a differential kind that determines the infinitesimal elements of the process of vibration.

"Is this state of the theory only transitory, or does it denote an actual advantage of the quantum theory? A theory should, indeed, determine the observable phenomena, but must not over-determine them. There are in the spherical wave, as we saw, only a definite number of determining elements or factors. Consequently a definite number of determining equations also suffices. Our integral equations of coupling for the energy and the moment of momentum do not, indeed, furnish a sufficient number of such equations. But they determine several essential factors of the ether vibration and allow the atom on the one side, and the ether on the other, the necessary freedom to behave in their appropriate manners, respectively, that is so that the atom suffers changes in stationary electronic orbits, and the ether undergoes vibrations. Of course, from the moment new empirical factors occur which do not fit into the scheme of the spherical wave with its finite number of parameters, effects such as onesided emission or similar phenomena, the theory must at once give up its general standpoint and must adopt new and cautious hypotheses, also, for example, about the nature of the transition from the initial to the final orbit," p. 263.

On p. 68 the author says that "it is impossible to picture as a physical reality a hydrogen ion carrying two positive charges. If a chemist should ever succeed in producing such a one, we should be compelled to declare all that follows in this book to be false."

The following passage, p. 201, is undoubtedly clear to the author; but it is likely to bother the chemist considerably. "If we recapitulate what we, arguing from the sharpness of spectral lines, have learned about the quantum treatment of the oscillator and the rotator and about the application of quantum methods to general systems, we get an entirely new type of natural phenomena. We therefore adopt the extreme view of the original Planck theory, according to which the quantum-favoured states lie solely at the limits of the elementary regions, whereas the interior of these regions remains quite free of phase-points. These quantised states are distinguished from all other possibilities as stationary states of the system by characteristic whole numbers; they do not succeed each other continuously but form a *network*. In the quantum orbits an electron moves, if undisturbed, permanently and without resistance, that is, without emitting radiation; the electron is thus, so to speak rendered immune by the quantum condition as regards the emission of radiation. *The phase-space, being the manifold of all conceivable states, including non-stationary states, is crossed mesh-like by the graph-curves of the stationary orbits. The size of the meshes is determined by Planck's constant h.*"

The next paragraph but one, p. 202, is more intelligible to the chemist. "Whereas solid bodies emit a continuous spectrum when they glow, we observe in the case of gases and vapours (except for isolated regions of continuous emission) line-spectra and band-spectra. The former belong to the atom, the latter to the molecule. Hence in a Geissler tube the hydrogen must first dissociate into atoms before its line-spectrum can appear. In the case of iodine vapour, on the other hand, the band-spectra disappear in proportion as the dissociation of I_2 into I progresses. The line-spectra consist of individual well-defined lines or complexes of lines; the band-spectra appear, if the dispersion is small, as toned bands (often accompanied by 'flutings') but they resolve under higher dispersion into a great number of neighbouring lines."

"The most direct test of Bohr's ideas, the one that is most free of theoretical elements, is the method of electronic impact. It was initiated by Franck and Hertz in 1913 and during the war it was developed in the United States particularly. At present it is being brought to a greater and greater pitch of perfection by Franck and his followers and is being applied to finer and finer problems," p. 337.

"From the point of view of theory, we must differentiate by a simple and unambiguous definition between arc and spark spectra. In our treatment of the series scheme we assumed that the atom under consideration was, as a whole, *neutral;* the jumping electron is then confronted by an atomic trunk of which the effective charge is $+e$. Following Bohr, we associate this case with the *flame* and *arc spectrums.* On the other hand, according to Bohr, to produce a spark spectrum we must have an ionised atom and (in the case of simple ionisation) an atomic trunk with an effective charge $+2e$. *We shall here always take spark spectrum as the system of emission of the ionised atom in the sense denoted by this theoretical distinction.* For the present, only cases of simple ionisation come into question, since only such have been observed—in general we shall hold in reserve for the system of the simply ionized atom the name 'first spark spectrum', for that of the doubly ionised atom the name 'second spark spectrum,' and so forth—in case these terms should prove necessary later," p. 372.

"W. Lenz has recognized a brilliant confirmation of the theory of bands in photographs of the fluorescence of iodine taken by R. W. Wood. Wood illuminates iodine vapour at a low pressure by means of the Hg-line 5461 (ground-member of the sharp subsidiary series). The iodine molecule, in absorbing the corresponding energy quantum $h\nu$, is brought into an excited ("*angeregt*") state. This state is associated with a perfectly definite value of the rotation quantum m. The iodine molecule re-emits the energy that is taken up, passing from the excited state to one of less energy. But the principle of selection allows only the transitions $m \rightarrow m-1$ and $m \rightarrow m+1$ (when the oscillation quantum and the electronic configuration change simultaneously). Hence the re-emission occurs as a doublet or, with due consideration to the circumstance that in the case of the non-harmonic oscillator, the oscillation quantum is capable of arbitrary jumps, it occurs, in a *system of doublets* scattered over the spectrum. Wood has observed about twenty such doublets. Each of them proclaims, as Lenz points out, in a very attractive way the sovereignty of the principle of selection over the rotation quantum; each shows us the process of birth of a partial band by two of its members. If, however, during the moment of absorption and that of re-emission we make the iodine molecules collide more frequently with each other (at higher pressure) or with foreign atoms (by adding inert gases), then other values of the rotation quantum are thereby produced. Each doublet then becomes multiplied to form a complete partial band: under these circumstances Wood's fluorescence photographs approach the ordinary band type," p. 430.

Wilder D. Bancroft

The New Theories of Matter and the Atom. *By Alfred Berthoud. Translated from the French by Eden and Cedar Paul. 23 × 15 cm, pp. 259. New York: The Macmillan Company, 1924. Price: $3.50.* The subject is presented under the following headings: introductory; the electromagnetic and electronic theory; the theory of relativity and mass; X-rays and atomic number; radioactivity and isotopism; Rutherford's atom and the transmutation of the elements; Bohr's atom and the theory of quanta; the constitution of complex atoms in relation to the emission of X-rays; atomic structure and chemical affinity.

Chemists will be interested in the paragraphs on high-frequency spectra, p. 117. "At the present time, all the elements which follow sodium in the periodic table have been carefully studied—excepting only gases of the helium group. A few years have thus sufficed to make us almost as fully acquainted with high-frequency spectra, as we are with far more complex light-spectra to which the attention of physicists has been devoted for a century.

"One of the first facts brought to light in these investigations is that an element's high-frequency spectrum is one of its characteristic properties—a property independent of its state of combination. The spectrum of brass consists of an exact superposition of the spectra of zinc and copper; that of potassium chloride is merely an aggregation of the spectra of potassium and chlorine. Hence it is possible to study such elements as chlorine and bromine, which cannot, in the free state, make up an anticathode. The gases of the helium group, which do not form any compounds, cannot be dealt with by this method.

"High-frequency spectra thus enable us to trace the elements through all their compounds, and give us direct proof that the individuality of the elements persists in all states of chemical combination. The high-frequency spectrum is a characteristic property of the atom, and differs from most of the other properties of that structure precisely in this persistence when the atom enters into combination. Although the changes (often extensive) which the elements undergo in chemical reactions show that the atoms are complex systems whose structure is subject to certain modifications, nevertheless the constancy of high-frequency spectra is a proof that these modifications do not destroy the individuality of the elements. They affect only certain regions of the atom, the peripheral regions obviously; and they leave unaffected the deeper parts of atomic structure, those in which the X-rays originate."

The author admits the possibility of all the elements being radioactive, p. 144. "If ordinary matter is in truth radioactive, and if it does give off rays analogous to those emitted by radium they can only have eluded observation through the speed of these radioactive transformations being a million times slower than that of uranium. In other words, the radioactivity of ordinary elements is as feeble when compared with that of uranium, as the radioactivity of uranium itself is when compared with that of radium.

"But we must not forget that it is only thanks to their high velocity that the α-rays and β-rays can be detected by a photographic plate, or by their ionising effects, or by scintillations. If they had a much lower velocity, we should doubtless still be unaware of radioactive transformations. An α-particle ceases to act in these ways when its velocity is still several thousand kilometres per second; and we have already learned that the β-rays of actinium and of mesothorium I elude observation because their velocity is too low. There is nothing against the supposition that ordinary matter may emit rays too soft to manifest their existence. This hypothesis can only be based on analogies, but it must not be forgotten that our methods of research are still imperfect, and that a slow disaggregation of the ordinary elements (a disaggregation analogous to that which occurs in radioactive substances) may be going on although the results elude our present powers of observation."

If we adopt Paneth's views that isotopes must be regarded as varieties of a single element and not as distinct elements, we may define an element, p. 163, as a substance characterized by a simple high-frequency spectrum or as a substance all of whose atoms have the same nuclear charge.

In the chapter on Bohr's Atom and the Theory of Quanta, the author says, p. 205: "Light, therefore, only acts on electrons by integral quanta. If the quanta are less than $h\nu_o$, they have no effect: if they are greater than this, the part of their energy which corresponds to the term $h\nu_o$ is expended in detaching the electron from matter; and the rest of their energy endows the detached electron with its velocity, and represents its kinetic energy.

"These phenomena are only conceivable on the supposition that the quantum of energy has extremely minute dimensions. Were it a considerable magnitude, we could not understand how an electron could monopolise its effects.

"Nevertheless, we must not blink the fact that Einstein's hypothesis is difficult to harmonise with the classical undulatory theory; that its acceptance would necessitate re-opening the whole problem of luminous phenomena, and would, in especial, invalidate the accepted explanation of interference. Naturally, therefore, most physicists regard it with considerable reserve, and are for the most part inclined to adopt a less radical solution. Besides, although Einstein's conception enables us to interpret some of the phenomena, it appears to conflict with others. The experiments of Lummer and Gehrcke have shown that the rays emanating from a source of light still interfere with one another when one set of waves lags behind another by several million wave-lengths—by more than a metre. Now we know that interference is only possible between coherent rays simultaneously emitted by the same radiator, but rays, one set of which has been artificially retarded as compared with another. Interference between distinct quanta successively emitted is extremely improbable. We shall have, therefore, to admit that the length of the train of waves representing a single quantum may exceed one metre. The train must also have a considerable width. Certain observations enable us to affirm that the light-rays emanating from a star and passing through one of the halves of the objective of an astronomical telescope interfere with those which pass through the other half. All these rays must, therefore, be coherent, and must belong to the same quanta. But if the quanta have such dimensions, they cannot pass through the pupil of the eye integrally. We should have to suppose that they divide on entering the eye, and that their fractions reunite in order to affect the retina. But in that case they are not indivisible! Finally, it is inconceivable that one electron can absorb an integral quantum having such vast dimensions.

"In view of these contradictions, Planck asked himself whether it might not be possible to free his theory of the supposition that absorption is discontinuous as well as emission, for discontinuous *absorption* is what gives rise to the chief difficulties. He has, in fact, been able to show that, as far as the laws of black radiation are concerned, whilst to account for them we must suppose that the emission of radiant energy takes place by quanta only, it is not necessary to assume that absorption is likewise discontinuous. In this revised form, the theory diverges less from received notions, and becomes more readily acceptable. We need no longer imagine the quanta to be strictly bounded in space and to be launched irregularly in all directions. We may assign to them whatever dimensions we please. It thus becomes possible to envisage each of them as a train of concentric waves, and this brings us very near to Maxwell's electromagnetic theory."

"Bohr's theory has thus endured the experimental test with remarkable success. Nevertheless, although this striking success must convince us that the theory is really accordant with the facts, we have to admit that it does not fully satisfy our minds. The difficulties already indicated as regards the quanta of energy, recur here in an aggravated form. In the case of an electron animated with an oscillating movement, the frequency of the waves emitted remains, just as on Maxwell's theory, equal to that of the oscillator, so that the absorption of radiant energy still exhibits itself as a phenomenon of resonance. But on Bohr's theory this is no longer what occurs. The leap of the electron, upon which the emission of electromagnetic waves depends, has no periodic character, and the frequency of the rays emitted has nothing in common with the frequency of the orbital movement of the electron. The frequency depends solely upon the quantity of energy given up—the reason being obscure. The absorption of light, which makes the electron pass from a narrower to a wider orbit, can no longer be assimilated to a resonance, and becomes incomprehensible. Finally, the movement of an electron free from radiation upon orbits having a definite dynamic equilibrium implies a most extraordinary structure for the electromagnetic field.

"Despite these grave difficulties, Bohr's theory represents a definite advance in our knowledge of atomic structure. The difficulties are inherent in the problem, for it is indubitable that classical electrodynamics are no longer valid in the interior of the atom. The physical significance of Bohr's postulates is still obscure, but the precision with which optical phenomena can be deduced from it shows that these postulates are a true expression of the mechanical laws of intraatomic movements," p. 216.

The author seems to have slipped up badly on p. 243. "Arrhenius' hypothesis was formerly criticised on the ground that it is difficult to see how simple solution in water can lead to the dissociation of a salt like sodium chloride, inasmuch as the formation of this salt is attended by the disengagement of a great deal of heat, which indicates that the components have a marked mutual affinity. This objection is still voiced from time to time, but it betrays a complete misunderstanding of the phenomenon. The objection was, indeed, refuted long ago, but the fallacy underlying it is now more plainly manifest than ever. In the formation of sodium chloride, the essential phenomenon, the one which is almost entirely responsible for the disengagement of heat, is the ionisation of the components, that is to say, the passage of one of the electrons of the sodium atom to the chlorine atom. The union of the ions thus formed so as to compose isolated molecules or a crystalline composite is no more than a secondary effect with but a very slight tendency to the production of heat." The difficulty with this otherwise convincing explanation is that most salts dissolve with absorption of heat and that the ionization of water is accompanied by an absorption of about 13700 cals per mol.

The author is quite ready to admit, p. 250, the present inadequacy of Bohr's model of the hydrogen molecule. "The researches undertaken in order to ascertain how far this model harmonises with the properties of hydrogen, have not afforded the expected confirmation. Debye has shown that it accounts satisfactorily for the dispersion of light in this gas. But that is the only favourable result which has been recorded. A study of the other properties of hydrogen discloses a complete divergence between theoretical forecasts and observed facts.

"It is not difficult to calculate the energy which would be required to distintegrate Bohr's molecule. Applied to the molecule-gramme of hydrogen, it amounts to sixty thousand calories, whereas the experimental measurements of Langmuir, Isnardi, Franck, and others, have given eighty thousand to ninety-five thousand calories. Thus the discrepancy, amounts to at least 25 per cent. Moreover, Bohr's molecule, thanks to the circular movement of the two electrons, must possess a magnetic moment parallel to the axis. Each molecule represents an elementary magnet which, in a magnetic field, has to place itself in a direction running along the lines of force. Hydrogen, therefore, ought to be paramagnetic, whereas in actual fact it is diamagnetic. Finally, Lenz has shown that the Zeeman effect in hydrogen is irreconcilable with the hypothesis that the two electrons revolve in the same direction.

"All these facts point to the conclusion that Bohr's molecule is not a true picture of reality. Other solutions have been proposed, but they remain extremely hypothetical. The models of the molecule of oxygen and nitrogen which Sommerfeld has constructed under the inspiration of Bohr's conception, have in like manner been found wanting when subjected to experimental contrpl.

"These failures give a clear indication of the inadequacy of our knowledge concerning the mechanics of the electron. We cannot hope for an accurate solution of the problem of the structure of atoms and molecluces until we are better informed as to the laws which regulate the equilibrium of their constituent particles. But this does not signify that we can afford to ignore the problem during the continuance of the present gaps in our knowledge. The laws will not disclose themselves spontaneously. The only way of discovering them is to go on elaborating hypotheses which can continually be checked by experimental fact, until at length the light comes." *Wilder D. Bancroft*

Fats: Natural and Synthetic. *By W. W. Myddleton and T. H. Barry. 25 × 20 cm; pp. xi + 182. London: Ernest Benn Limited, 1924. Price: $4.00.* The chapters are entitled: the nature of the oils, fats, and waxes; examination of the fatty acids derived from the oils, fats, and waxs; oil extraction and purification; the fatty acid industry; catalytic hydrogenation; physical examination of the synthetic fats; chemical examination of raw material and hydrogenated product; soap manufacture; candle manufacture; margarine manifacture, chocolate fats, shortening fats; control of the formation of the "new acids of hydrogenation"; complete synthesis of fats.

In the preface the authors say:

"The synthetic processes dealt with are for the most part concerned with the conversion of the liquid oils into solid fats by catalytic hydrogenation. The more complete syntheses from glycerine and fatty acids which have been in turn built up from other material have been examined briefly, but their interestf rom the commercial point of view is at the present time problematical. The hydrocarbons of petroleum oils have suggested themselves as a suitable starting-point in the synthesis of fatty acids, but the chemical treatment required is costly and the yields are poor. It is doubtful whether the supply of petroleum hydrocarbons is sufficiently great to justify us in counting on them as a source of more than temporary importance.

"The hydrogenation process allows of the conversion of vegetable oils, the stock of which is annually renewable, and the fish oils, of which there is a continuous supply, into solid white fats of any desired consistency, free from the highly saturated compounds which give rise to the characteristic and oftentimes objectionable odour and taste of the original oil. The products are much more stable than the raw material, and do not undergo appreciable deterioration during storage and use. Many industries find the fats of greater value than the liquid oils, but the utilisation of the synthetic product is by no means a simpler matter. It is no exaggeration to say that considerable difficulty has arisen in every industry in which the hydrogenated oils have been called into use.

"The authors have approached these difficulties through a study of chemical composition. The difference in chemical composition between the natural and the synthetic fats has been demonstrated by tables of analyses, and the changes taking place in the oil during the progress of hydrogenation have been illustrated diagrammatically."

"A fat is merely an oil of such high melting-point that it is solid at ordinary temperatures: in some cases—as for example, palm oil—the melting-point is below the usual temperature of the tropical countries where it is produced but above that of temperate countries such as Britain, where it is largely used. The term oil is, however, still applied to it, though it is to all intents and purposes a fat in this country," p. 1. The waxes of vegetable and animal origin may be considered as "closely related to the fats in that they are compounds of similar organic acids with an alcohol of higher molecular weight, however, than glycerine. Whilst the oils and fats are found within the cells of plant and animal tissues, and their extraction involves the preliminary breaking down of the cell walls, the waxes are characterically exudation products or excretions of cells, those of animal origin being exuded into the body cavities. Mineral waxes are related to the mineral oils, in the same way as the vegetable fat is related to the vegetable oil," p. 2.

"As already mentioned, the oil cake is an important by-product of the oil industry. The cakes from different seeds naturally have somewhat different nutritive properties. Linseed oilcake is the most popular in England, being a good all-round cake either for fattening or milk-producing. The arachis and coco-nut cakes are especially valued for their milk-producing qualities. The cake from palm kernel is not enjoyed by cattle on account of its woody and unpalatable taste, but it was used in enormous quantities in pre-war Germany as a pig food. The use of cotton seed has been the subject of much controversy. The American decorticated cake is a very highly concentrated food and rich in abluminoids, whereas the English cake is largely produced from undecorticated seed, and is therefore a more bulky food and not so rich in albuminoids. It possesses, however, certain astringent properties which are valuable in view of the soft lush grass on which the English cattle invariably feed," p. 25.

As in the case of the animal oils, the climate has an influence upon the composition of menhaden oil. "The oil from fish caught in the cold Northern waters contain a lower proportion of unsaturated glycerides than that from fish caught in the warm waters off the Florida coast," p. 40. Menhaden oil, "when exposed to air in a thin layer, dries in a manner similar to linseed oil, but not to so hard a film. It is, therefore, specially valuable when used in conjunction with linseed oil for paints which are subjected to wide temperature variations. It is also stated that paints containing it are less liable to blister," p. 40.

On p. 50 it is stated that "by using calcium oxide it is possible to effect complete saponification; but a large excess of the calcium oxide must be present and the time taken is considerable. The calcium soaps are insoluble in water and have no extensive application, so that a large amount of a mineral acid must be used to recover the fatty acids from the insoluble calcium soaps." We are usually told that lime works more rapidly than soda and that less is required. There is something wrong here. '

"We have termed the mixture of solid unsaturated acids formed during hydrogenation the 'new acids of hydrogenation,' because it does not appear advisable to us to apply the name 'iso-acids' to a mixture of substances the exact nature of which has not been shown conclusively," p. 20. "On comparing the natural tallows with the synthetic products of hydrogenation we find that the presence of the new acids of hydrogenation coincides with a marked decrease in lathering power. In whale and the fish oils, in which there occur unsaturated acids containing large numbers of carbon atoms, there will appear amongst the products of hydrogenation corresponding amounts of unsaturated acids of very high molecular weight. Soaps formed from such acids are very slightly soluble even in hot water, and the surface-tension effect of the dissolved portion is very poor indeed. Hardened whale and fish oils are thus very unsatisfactory material for soap making," p. 123.

"Candles are made of combustible solids, which melt at moderate temperatures to form liquids which are sufficiently fluid to allow of their supply to the burning zone through a porous wick. The region of flame is thus restricted, and the wick must be modified with regard to texture and porosity according to the nature of the liquefied substance, so that a regulated flow to the flame is assured. When considering the suitability of a fatty material for candle manufacture, it is necessary to bear in mind that the burning properties of the material will depend largely upon the form of the wick and the consequent type of flame produced.

"The mechanism of the wick is, therefore, of considerable interest. Cotton is the standard basis of the candle wick, and it is frequently plaited with a slight strain on one strand, so that when the support given by the solid candle material is taken away by gradual melting the end of the wick curls over and burns away at the edge of the flame as the candle burns down. The shape of the flame is also modified in this way, and a less smoky burning is affected.

"A preliminary treatment known as pickling is necessary to prevent the rapid combustion of the wick, and at the same time to produce a vitrification at the end which curls over to the edge of the flame so that it drops off easily. The pickling process consists in steeping the wick in a solution containing salts, such as borax, potassium nitrate, or ammonium phosphate. The excess of the solution is removed by placing the prepared strands in a centrifuge. A final drying in a heated chamber completes the necessary preparation. Fine metallic wires have been woven into the cotton wick in some cases, so that a bead of the metal may be formed at the tip of the wick to weight it down and produce a curl. Metallic salts which give a bead of the metal in the reducing gases of the flame have also been used to achieve this end."

One can hardly agree with the statement, p. 145, that "the second type of emulsion is very unstable and contains the water in very fine particles surrounded by oil. Only very powerful emulsifying agents are capable of rendering this form permanent."

"It might be judged from the preceding that the synthetic fats could fully replace the natural products. Such, however, is not the case. The whole question of the mechanism of nutrition has acquired a new interest in the discovery that, in addition to a sufficient supply of food for the material renovation of the organism and the supply of energy, certain substances provisionally known and described as "vitamins" are essential if the body is to utilise efficiently the food-stuff supplied. These exist in minute quantities in the animal fats and oils and are apparently destroyed in the process of hydrogenation," p. 149.

Wilder D. Bancroft

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TEMPER COLORS[1]

BY C. W. MASON

Ever since the time of Newton, when the nature of the interference colors produced by thin films was first recognized, it has been generally assumed that the so-called *"temper colors" of metals were examples of this phenomenon.*[2] This view is widely held in works on Metallurgy and the change of color as tempering continues is considered to be due to the increasing thickness of the oxide film formed. The influence of temperature and of time on the film production and on the reactions of tempering in the metal itself are comparable, so that temper colors serve as a more reliable guide to tempering than could information as to temperature alone.

The above explanation has been put in question by Mallock[3], who says: "I had thought, and I believe it has generally been assumed that the colours of tempering were instances of the ordinary interference colours of thin plates, but the following simple experiment seems to prove conclusively that this cannot be the true explanation. If the colours were due to a film of appropriate thickness, a reduction of that thickness ought to change the colour; the blue should change to green, orange to yellow, and so on. I found however, that if the tempered steel surface was gently polished, until the clean surface of the metals was reached, there was no change of colour during the process, the blue remaining blue, and the yellow yellow, until the whole of the colour was removed. The intensity of the colour decreased as the film became thinner, but the character remained the same."

This observation, unquestionably a correct one, has raised the whole problem again, and later workers have accepted Mallock's conclusion without sufficient examination of its justifiability, so that we have a number of writers ascribing the colors to selective reflection, diffraction, or resonance phenomena because they cannot be due to thin films. Before ruling out this explanation, however, it is desirable to survey the evidence for it rather carefully, and the present paper was written with this in mind. Previous study of various types of structural colors[4] involved the development of criteria by which the different kinds might be distinguished from each other, and these served as a basis for the study here presented.

The most powerful argument against the non-structural basis of temper colors is the fact that the same sequence of color may be observed, wholly or in part, from a number of different metals acted upon by a number of

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[1] This paper is a necessary corollary of experiments supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] In the seventeenth century metal powders were given various colors by heat treatment, for use in decoration. Beckmann: "History of Inventions," 2, 160, (1814).

[3] Proc. Roy. Soc. 94A, 561 (1918).

[4] Mason: Jour. Phys. Chem. 27, 201, 401 (1923).

different gases to form films of widely different chemical nature. Silver iodide or sulphide, copper or iron oxides, in fact, any case where a metal is slowly acted upon by some substance capable of forming an appreciably transparent and coherent product on its surface, will exhibit, to a greater or less degree, the same sequence of colors as the action proceeds.

The colors formed are, in order, as follows: pale yellow, straw yellow, red orange, purplish red, indigo, blue, green, yellow, orange, purplish red, blue, green, purplish red, etc. with perfect gradation of each into the next. While the colors which develop first are very similar in the different cases, the range of the series is limited by various factors, so that the colors produced by more extended action upon various metals do not correspond strictly to each other. The general likeness in the series of colors produced by surface action is so marked, however, that the identical nature of those obtained on different metals would be self-evident at once, were it not for this dissimilarity under further action. The probable explanation of this will be discussed later.

Another very characteristic property of temper colors is the change in hue which they exhibit with changing angle of incidence. This is best observed when the color is uniform over a considerable area, or where some definite spot on the surface can be watched without the observer's attention shifting with the color. Naturally, there is a marked decrease in saturation as the angle of incidence increases; but, accompanying this, the hue itself changes, in a manner that is definite for a given color, whatever may be its chemical nature, and the color produced, to put it briefly, is one immediately preceding the original color, in the series given above. In other words, the color observed at *grazing* incidence is one which corresponds to that obtained by somewhat less chemical action on the metal, seen at *vertical* incidence. For example, purplish red will change to orange at grazing incidence, orange to pale yellow, etc.

The character of the color sequence, and the change with angle of incidence, of course, are the foundation of the thin-film theory of the origin of temper colors. In terms of this theory, the observed facts may be described thus: As chemical action proceeds, increasing thickness of the film formed gives rise to a series of interference colors (Newton's series) increasing in order with the extent of the action. As the angle of incidence is increased, these colors change to ones preceding them in the series, that is, to colors of *thinner* films.

The concordance, as far as it has been carried, is adequate, and the only serious discrepancy is that stated above by Mallock. The thickness of the color film on metals has not been measured directly, but soap films showing similar colors are of the order of magnitude of 0.25μ, for purple to deep magenta, (of the first order)[1], which corresponds to a common temper color of steel, and if the index of refraction of the film itself (perhaps 3.+) is taken into account, this would indicate an oxide film only about 0.1μ thick. It is hardly to be expected, therefore, that "polishing" with abrasive particles of

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[1] Boys: "Soap Bubbles," 149 (1912).

order of magnitude of the thickness of the film itself, or more probably, several times this, should do anything except plow off the film without any progressive and uniform thinning, any more than in "rubbing down" a varnished surface with coarse sand paper. If the polishing were of the nature of surface flow, uniform reduction of the thickness of a film of brittle and imperfectly adherent oxide is not very probable. Mallock has not shown that it is possible to carry out his polishing experiment successfully in the case of a color that is admittedly due to interference. Chemical attack would be much more likely to prove something, one way or the other.

When a brilliant blue temper color on highly polished steel is covered with a very dilute solution of nitric acid, the color does not disappear all at once, but instead passes through a *sequence* of colors, the exact reverse of that which is observed when the film is forming. It is possible to stop this action at any point by washing off the acid, and comparison of treated and untreated color films leaves no question as to the above facts; the blue may be changed to reddish purple, or, by longer exposure to the acid, to straw yellow. On reheating such a specimen, the original colors may be wholly or partially restored, passing through the sequence in the reverse direction. The above behavior may be duplicated with oxidized copper, the same lowering of the order of the color being observed. Nitric acid is not suitable, but dilute hydrochloric acid (concentration determined by trial) attacks the oxide slowly and thins down the film evenly.

Study of the colors of thin films with polarized light shows that at angles of incidence greater than the "polarizing angle" their color, for vibrations in the plane of incidence, is complementary to that for vibrations normal to this plane. This phenomenon is readily observable in the case of the "temper colors," and points definitely to their identity with thin film colors, particularly since all hues of the series show this behavior, a fact hardly to be expected from a group of substances showing selective reflection.

Incidentally, accurate measurement of the "polarizing angle" ought to furnish a means for determination of the approximate index of refraction of the film ($n = \tan.$ angle of incidence), and possibly for its identification. This angle is large, and indicates a very high index of refraction for the surface film.

Mallock[1] studied the behavior of temper colors with polarized light: "The colours of tempering are best seen by polarized light, and their intensity is greatest at the angle of maximum polarisation. When so observed the blue changes, as the angle of incidence increases, through reddish-purple to a dark orange and finally to a straw yellow. The yellow and orange parts, on the other hand, change but little, becoming rather more intense at the angle of maximum polarisation; but the whole surface, which has been coloured by the tempering, assumes a nearly uniform yellow when the incidence is large. Thus the blue moves toward the red end of the spectrum, while the orange does the opposite, and although similar changes occur in the case of the higher order of Newton's rings, the thickness of plate required

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[1] Proc. Roy. Soc. 94 A, 561 (1918).

is far greater than that which produced the colours of tempering. It would seem probable, therefore, that the latter colours are due to some form of selective opacity depending on damped molecular periods comparable with the wave period,[1] rather than on a structure comparable with the wave-length."

As regards the change of color with increasing angle of incidence, Mallock's own report corresponds perfectly to the behavior of a film of a thickness corresponding to about blue of the second order. It is *not* a question, however, of the "end of the spectrum" toward which the colors move. People have been confused by this in the case of iridescent feathers. Thin-film colors change to those *corresponding to thinner* films as the angle of incidence is increased, and this is exactly what Mallock observed. As he says, the blue changes "through reddish purple to a dark orange and finally to a straw yellow," precisely as does a thin-film color of the same hue. This, of course, is the reverse of the sequence of color changes which takes place when the film is forming (growing thicker).

His statement regarding the thickness of film necessary is open to question, for the colors he describes apparently are in the second and upper first order, and for these only a very thin film is necessary (probably less than 0.3μ).

If Mallock's studies had been made with ordinary unpolarized light, the difference between the behavior of temper colors and that of substances showing selective metallic reflection (surface color) would have been more apparent, for while thin film colors change markedly with unpolarized light as the angle of incidence is increased, surface colors from substances showing selective reflection (magenta, malachite green, crystal violet, etc.) exhibit little if any change in hue under these conditions.

Any theory of selective reflection as the cause of the colors necessitates postulating several differently colored oxides of each metal, formed always in the same sequence and, in some instances, of two or more oxides showing the same selective reflection. Apparently there is no direct evidence to support such a series of compounds. Beilby[2], in describing the temper colors of steel, ascribes the straw yellow which first appears to a thin film of Fe_2O_3; a somewhat thicker film is red, the color of thin films of hematite; the brilliant blue which next appears is considered to be the surface color of the Fe_2O_3, which is now so thick as to be opaque, and to show no body color. However, no massive oxide of iron exhibits a blue surface color, and the identical appearance of thin films of *colorless* substances (e.g., AgBr) is evidence that the series observed does not require such postulates for its explanation.

Then too, presence of two whole "orders" of color can hardly be explained on the basis of anything other than thin films. In the case of some of the

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[1] This must be true of all pigment colours, but something more is required to explain the dependence of the colours of tempering on the angle of incidence, a feature which is strongly marked also in the case of many of the aniline colours when examined as dry films by reflected light. (Mallock.)

[2] "Aggregation and Flow of Solids," 62. (1921.)

more readily oxidized metals, copper, for example, three "orders" or more may be observed. The resemblance to the well-known sequence of thin-film colors is so striking that it is natural that the great body of opinion on this subject inclines to this explanation, and it is unfortunate that Mallock's experiment, inconclusive as it is, should have been allowed to outweigh such obvious resemblances[1].

Another experiment which adds a little to the thin-film explanation, depends on the fact that when exposed thin films are brought in contact with a medium of index of refraction near their own, the intensity of their colors is markedly decreased, and vanishes if the index of the film and of the external medium are identical. On covering a series of "temper colors" on steel with a liquid of index of refraction greater than 1.8, the diminution of intensity of reflection is very evident, as compared with that of the uncovered film. Care must of course be taken to eliminate effects due to reflection from the surface of the liquid itself. Since any oxide which may exist probably has an index of refraction at least as great as that of hematite (*ca.* 3.0), complete disappearance of the color is not to be expected; but the behavior observed corresponds very well to that of a color-producing thin film. Where the index of refraction of the film is more nearly matched, the effect is very striking; burnished silver becomes coated with a film of AgBr on exposure to bromine vapor, and colors corresponding to the first three complete orders and part of the fourth may be recognized. Covering the surface with a liquid of about 1.8+ index of refraction causes almost complete disappearance of the colors. [n AgBr = 2.2]

On the other hand, selective reflection is ordinarily accompanied by anomalous dispersion, and substances exhibiting it show marked change in color with change in index of refraction of the surrounding medium. This is very strikingly exemplified by the solid dyestuffs, but there is no indication of it in the case of any of the temper colors.

The change of color with angle, exhibited by films on metal surfaces, is not as marked as that observed with oil films on water; this is on account of the high index of refraction of the metallic oxides, sulphides, halides, etc., in question. Even when the light is grazing, the angle *in the film* is small (less than the critical angle), and, as a consequence, the retardation is less than if the light traveled a path more inclined to the normal. Newton[2] recognized this general property and its application to films on metals: "I have sometimes observed, that the colours which arise on polished steel by heating it, or on bell-metal, and some other metalline substances, when melted and poured on the ground, where they may cool in the open air, have, like the colours of water-bubbles, been a little changed by viewing them at divers obliquities, and particularly that a deep blue, or violet, when view'd very obliquely, hath been changed to a deep red. But the changes of these colours are not so great and sensible as of those made by water. For the

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[1] Even Wood [Phil. Mag. (6) 38, 98 (1919)] seems to have been put off the track by the "polishing" experiment.

[2] "Opticks," 194 (1721).

scoria or vitrified part of the metal, which most metals when heated or melted do continually protrude, and send out to their surface, and which by covering the metals in the form of a thin glassy skin, causes these colours, is much denser than water; and I find that the change made by the obliquation of the eyes is least in colours of the densest thin substances."

Mallock suggests that the colors are due to diffraction or at least he points out that in some instances the diffraction systems that he was studying gave a sequence of colors very close to that of the colors of tempered steel, and Hinshelwood[1] states definitely that the colours are due to diffraction. "That the colours shown by oxidized copper and by tempered steel are due to diffraction was pointed out by Mallock, who found that a film of given tint could be ground away while retaining its colour, which must therefore be dependent not upon its thickness, as it would be if interference were the cause, but upon its minute structure." Corroborative evidence is cited by Raman.[2]

Any theory of diffraction as the cause of temper colors is open to the cogent objection that if this is the case the colors ought to disappear in uniform light, and ought to be observed, not in the direct line of reflection, but to the side of this. Neither is the case.

Hinshelwood[3] gives some experimental studies of the oxidation of copper, which are of interest in the light of the preceding pages: "When the surface of a metal is exposed to the action of a gas with which it reacts chemically, brilliant colour phenomena are frequently produced. In some cases the colours are recognised as diffraction colours, produced by the scattering of light in the surface film, and not as simple interference effects. When this is found, the film must have a more or less complex structure, fine-grained compared with the wave-length of light, but of a coarse-grained granular nature compared with molecular magnitudes. The work of Beilby has drawn attention from other points of view to the complex structure which the surface layers of metals, or thin films of metals, may assume.

"It seems to be of considerable importance to correlate the chemical activity of such surface films with their structure, in view of the bearing this correlation may have on the problems of heterogenous catalysis. A first attempt in this direction is made in this paper, the reaction investigated being the oxidation and reduction of a copper-copper oxide film on the surface of metallic copper.

"The general nature of the phenomena observed is as follows: When bright, rolled copper foil is exposed to the action of oxygen gas at low pressure, and at 200°-300°C., a film of oxide forms on the surface, and, as oxidation proceeds, the velocity of oxygen absorption diminishes considerably, owing to the difficulty of penetration of the oxide film. The surface assumes various tints, all of which, however, are quite faint, finally becoming black. Its metallic lustre is retained throughout. After reduction, a second oxidation is brought about very much more readily than the first, and the surface

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[1] Proc. Roy. Soc. 102A, 322 (1923).

[2] Nature. 109, 105 (1922).

[3] Proc. Roy. Soc. 102 A, 318 (1923).

assumes a new series of tints, brighter than the first, and even qualitatively distinct from them. Successive oxidations and reductions take place more and more readily until, ultimately, a limiting rate appears to be attained, which may be some hundreds of times greater than the original rate. As the surface becomes more and more active chemically the diffraction colours simultaneously increase in brilliancy. Ultimately a permanent colour sequence, with tints of great brilliancy, is established, which may be traversed time after time. The surface loses its metallic lustre, and when in the fully *activated condition the copper is salmon-pink in colour.*

"During the activation process the structure of the surface film seems to change in the following way: At first the surface layers of the copper foil are compact as a result of its mechanical treatment; during the successive stages of activation by alternate oxidation and reduction, the copper atoms in the surface film are able, under the influence of surface tension, to aggregate themselves more and more completely into small discrete units in what Beilby calls 'open formation,' and the film assumes a granular structure freely permeable to oxygen. From the experiments to be described it is possible in principle to determine the size of these small granules, and although there are difficulties in the way of finding accurate values, it emerges clearly that the order of magnitude of their diameter is only a small fraction of 1μ. The view has been expressed that metallic grains as small as this assume a spherical form.[1]. But Sir George Beilby has kindly pointed out to me that the evidence of microphotographs shows the film to be lenticular in structure. In the last section of this paper the magnitude of the granules is calculated, for the sake of simplicity, on the assumption that they are spherical. The radius thus determined will be their mean or 'effective' radius.

"Each small unit of copper will be oxidised independently, and the extent to which it is converted into oxide determines the colour of the diffracted light. The amounts of oxygen absorbed, corresponding to various well-marked steps in the colour sequence, has been determined, and may, incidentally, be of interest in connection with the optics of the phenomenon.

"There is a curious difference between the phenomena observed during reduction and those observed during oxidation, which suggests an interesting mechanism for the gradual activation of the film."

"In the oxidation of copper, the brilliancy of the colour increases *pro rata* with the chemical activity, the granular film which most effectively scatters light presenting the largest surface to the action of the oxygen. When fresh copper is oxidised the colours are faint and the sequence is not constant, but is usually silvery or steely, pale straw, violet, black. The permanent colour sequence is purple, blue, green, very light green, (almost yellow), purple, blue, black. These are very brilliant, except the second appearance of purple and blue; they appear uniformly and are quite constant in hue from time to time. . . . .

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[1] Maxwell Garnett: Phil. Trans. 205 A, 279 (1906).

"The oxidation of an active film must be imagined to consist in the independent oxidation of each of the small granules composing it, a layer of oxide being formed on the surface of each and extending inwards. The size and composition of each thus changes, and consequently the colour of the film alters. Thus, when the granules consist of approximately one-third oxide and two-thirds copper, the colour of the scattered light is bright blue. Within the boundary of each granular unit of copper or of copper oxide there is no reason to doubt that the density of the material is normal, the low mean density of the film being due to the spacing of the granules.

"The effects observed during reduction differ in a remarkable manner from those observed during oxidation. No diffraction colours appear when a black film is reduced, the colour of the film at any stage of reduction being simply a shade of brown produced by the combination of the red colour of the copper and the black of the oxide."

Hinshelwood's experiments were duplicated roughly by oxidizing burnished copper in air and reducing it in illuminating gas, this being repeated several times. The color sequence produced by the oxidations was reversed by the reduction, and development of the matte character of the surface was very apparent. This was retained after reduction, and resembled unburnished electrolytic copper. The microscopic appearance of the surface corresponded with this; a finely reticulated or granular structure was apparent, seemingly existing not as bosses, but rather as microscopic fissures in the surface. On repeating the oxidation and reduction a considerable number of times the oxide film became so brittle that it flaked off. This behavior on a coarse scale is consistent with the development of a reticulated microscopic structure on alternate reduction and oxidation.

Beilby[1] discusses at some length the development of porous or lenticular character in surface films on metals, and evidently some such structure plays a part in the optical behavior of the material, as well as in allowing the oxidation to proceed instead of "passivation" taking place after the first formation of the oxide film.

The color sequence which Hinshelwood reports ("purple, blue, green, very light green, purple, blue, black"), corresponds to the series of thin-film colors of the second and lower third orders; the first order (yellow, red) is obscured by the color of the copper, and the upper third by the opacity of the oxide formed. The increased brilliancy which he observed is due no doubt to the matte surface developed on the copper by the oxidation and reduction, since the same apparently enhanced depth of color is observable on other metals which are only coarsely polished and then tarnished. Such matte character enables the color to be observed through a relatively wide angle of vision instead of at the angle of reflection only, and also decreases the "diluting" effect of the light reflected through the film from the metal surface beneath it. Both of these effects would serve to increase the apparent brilliancy as ordinarily observed. At the same time the specular metallic lustre is mark-

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[1] "Aggregation and Flow of Solids," (1921).

edly lessened, and the resemblance to pigment coloring of the surface is heightened. These factors also govern the appearance of any matte metal surface, not covered by a color film. The differences between electrolytic and burnished copper or silver are striking enough to emphasize their significance in the case of the colors observed when the metals are tarnished.

It is pcssible to overlay such a matte metal surface by a thin film of varnish, prepared by allowing a drop to spread and harden on still water. Here we have a film which unquestionably owes its color to interference, yet when it is brought into contact with the metal the appearance is identical with that produced by tarnishing. Similar films on burnished metal show very much less vivid colors. On the whole, the brilliancy of the colors sometimes observed does not appear to indicate any different origin from those of burnished metal surfaces.

Raman[1] seems to have been troubled by this appearance, and in his paper mentions another property of the colors which throws light on their physical nature, and is closely related to some of Hinshelwood's ideas on the structure of the surface film which causes them:

"The well-known and characteristic tints that appear on the surface of a tarnishable metal when it is heated in contact with air have been usually regarded as interference colours due to the formation of a thin film of oxide on the surface of the metal. The correctness of this explanation has recently been questioned[2] and rightly so, as a continuous film on a strongly reflecting surface cannot on optical principles be expected to exhibit such vivid colours as those observed. I have recently made some observations which shed a new light on this subject. It is found that the *missing colours* complementary to the tints seen by reflected light appear as light *scattered* or *diffracted* from the surface of the metal. In other words, if a plate of blue-tempered steel be held in a beam of light and viewed in such a direction that the regularly reflected light does not reach the eye, the metal shows a straw-yellow color and not the usual blue. It will be understood that the scattered light, being distributed over a large solid angle, appears much feebler than the regularly reflected colour, and in order to observe the effect satisfactorily the metal should have a smooth polished surface before being heated up. Scratches and irregularities show the ordinary colour of the film, and not the complementary tint. The most attractive effects are those exhibited by a heated copper plate, both on account of the vividness of the colours and on account of the ease with which the surface can be given a satisfactory polish.

"It is clear from the observations mentioned above that the colours under discussion are in the nature of *diffraction effects* arising from a film which is not continuous, but has a close-grained structure. Interesting effects are observed when the surface of the illuminated plate is viewed through a nicol, the colour and intensity of the scattered, as well as of the regularly reflected, beams varying as the nicol is rotated about its axis. The most striking

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[1] Nature, **109**, 105 (1922).

[2] Proc. Roy. Soc. **94** A, 561 (1918).

effect is obtained when the direction of observation is nearly parallel to the surface of the plate. The scattered light in this case is nearly completely polarised, and the color of the regularly reflected light changes nearly to its complementary when the nicol is turned through 90°. The phenomena strongly recall to mind the observations of R. W. Wood[1] on the colours of a *frilled* collodion film on a silvered surface, which have been discussed by the late Lord Rayleigh[2], and it seems probable that the explanation of the phenomena will ultimately be found to be somewhat similar in the two cases."

This letter moved the editor of Nature to append the following note: "Mr. Mallock has shown that the colour of the oxide film is an *intrinsic* property of the material of which it is composed, and the material retains this property as it is gradually ground down from its original thickness to the vanishing point. Sir George Beilby's observations have confirmed this, and have further shown that the film is an aggregate *in open formation* through which oxygen molecules can penetrate to the metallic surface. For each temperature above the temperature range the thickness of the film is determined by the porosity of the aggregate to the oxygen molecules at that temperature. Direct experimental observations have shown the part played by *time of heating* at any given temperature. For example, at 275°C, a deep purple was reached in ten minutes, and this changed to blue from the margin inwards during a further period of twenty minutes. It was thus shown that the watch-spring blue, which could immediately be produced by a temperature of 300°C, should also be produced by heating at 275°C for thirty minutes. Sir George Beilby's view is that the *intrinsic* colours of the films which are produced at different temperatures result from changes in molecular aggregation in relatively open formation of a similar nature to those which have been shown to occur in thin metal films, *e.g.* gold. This is referred to in his recently published volume entitled "Aggregation and Flow of Solids", sections 3 and 10."

Although, as Raman points out, the "temper colors" of metals are similar in some respects to those of "frilled films," it must be borne in mind that this does not preclude their explanation in terms of ordinary thin films. The distinctive feature of frilled films is their power of scattering light of complementary color to that which they reflect directly. It is admitted that the color of the light reflected directly from such a film depends on the thickness of the film in a manner identical with that of a non-frilled thin film.

The fact that the light scattered by frilled films is complementary in color to that directly reflected by them renders it also dependent on the thickness of the film, and points to its being related to the transmission color, which is also complementary to the directly reflected color, though less saturated. Probably the "frilling" serves, in some way not definitely understood, to scatter the colored light which would be transmitted by a film not

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[1] "Physical Optics," 172 (1914).

[2] Phil. Mag. (6) 34, 423 (1917).

backed by a reflecting surface, and at the same time eliminates the loss in saturation due to the reflection from the metal surface itself.

The effect of "frilling," whatever its real explanation may be, is manifest in the scattered light, and is viewed from a point considerably out of line of direct reflection best when the illuminating beam is normal to the surface and the line of vision is grazing. Under such conditions the "temper colors" exhibit more or less scattering of a color complementary to that which they reflect, but this scattering is not nearly as marked as in the case of the collodion films of Wood, and under ordinary conditions plays no part in the appearance which is observed on a piece of metal.

Any change in a thin film which will increase its opacity somewhat without decreasing the reflection from the outer surface will result in increased brilliancy of color[1] and the frilling no doubt accomplishes this to some extent. The naturally strong absorption of metal oxides is also an important factor and helps to account for the vivid appearances observed, which Raman says "a continuous film on a strongly reflecting surface cannot on optical principles be expected to exhibit." The effect of absorption in the film itself is exemplified by the case of asphaltum films on white paper. Such films, thin enough to give interference colors, are distinctly brownish by transmitted light, and the colors seen against a white background are distinctly more brilliant than those of gold-size films, which appear colorless by transmitted light. In a sense, this is as if the asphaltum film were serving as its own dark background, with the enhancement of color that accompanies such an arrangement.

A similar appearance is exhibited by "burned out" or old incandescent lamp bulbs in which the metal filament has been volatilized and deposited on the glass. This deposit probably consists of the metal itself, in a very fine-grained and uniform layer. Its opacity is very marked, yet the colors of the deposit are very striking, and resemble closely the temper colors of steel. Where the deposit is considerably thicker it appears almost opaque, and of a steely metallic appearance by reflected light. Here again we have a strongly absorbing substance showing colors in thin films rather more brilliant than in the case of colorless substances.

On the whole, it appears that the objections raised to the thin-film theory of temper colors may be rather readily reconciled with this view, while any conclusive evidence against the theory, or in favor of other explanations, seems to be lacking; on the other hand, these latter are open to serious question.

The conclusions of this paper are as follows:—

1. Temper and similar colors of metals are due to interference of light, reflected from the two surfaces of a more or less transparent film of a compound of the metal formed on its surface, in a manner corresponding precisely to Newton's rings.

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[1] Wood: "Physical Optics," 171 (1911).

2. Any reticulated or granular structure of the film adds to the vividness of the color.
3. A moderate degree of opacity of the film enhances the color.
4. The color of the material of the film itself obscures the interference colors in the case of thicker films.
5. Properties similar to those of "frilled films" are probably due to the fine structure of the film, but these are of minor importance in the appearances observable under ordinary conditions.
6. Diffraction or selective reflection are inadequate as explanations of the nature of the colors, and inconsistent with their behavior.

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ON THE INFLUENCE OF THIN SURFACE FILMS ON THE EVAPORATION OF WATER

BY GUNNAR HEDESTRAND

It is known from the work of Rayleigh,[1] Devaux,[2] Langmuir,[3] Marcelin,[4] Adam,[5] and others that certain oily substances such as the higher fatty acids, alcohols, and esters readily spread upon a clean water surface forming thin invisible films. From a careful study of the properties of such films many interesting facts have been found.

All evidence is in favour of the assumption that these films are one molecule thick, and that by measuring the area occupied by a known amount of the oily substance, the cross-section of one molecule can be calculated. A comparison of the thickness of the film with the square root of the cross-section of one molecule proves that the oil molecules are oriented vertically to the water surface. According to Langmuir the chemically active groups of the molecules, carboxyl, amino group, double bond, etc., are directed downwards towards the water, and the hydrocarbon chains upwards, parallel with each other.

The surface properties of the water are altered by the oily contamination, the surface tension being diminished, but this decrease does not occur, till the close packing of the oil molecules begins. After the closely packed unimolecular layer is formed, there is no further decrease of the surface tension.

As a decrease of the surface tension means a decrease of the forces between the water molecules in the surface, it might seem probable that oil films would increase the rate of evaporation. However, by spreading a layer of oil on the water we introduce a resistance, which the water molecules have to pass, before they can escape to the gas phase.

It was suggested to me by Professor Donnan, to try to determine in what way these "dynamic" conditions of the water surface are affected by the presence of an oil film.

1. Experimental Methods

The real rate at which the water molecules escape from the surface, is the rate of evaporation in a vacuum. On account of the high vapour tension of water, however, there are great difficulties in determining this rate, for in a vacuum the evaporation would be so rapid that the water would cool rapidly and soon freeze.

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[1] Rayleigh: Phil. Mag. (5) 48, 331 (1899).

[2] Devaux: Am. Rep. Smithsonian Inst. 1913, 261; Soc. Franc. Phys. 55, 3 (1914); 57, 3 (1914).

[3] I. Langmuir: J. Am. Chem. Soc. 39, 1848, (1917).

[4] Marcelin: Ann. Phys. (9) 1, 19 (1914).

[5] N. K. Adam: Proc. Roy. Soc. 99A, 336 (1921); 101A, 452, 516 (1922).

In the method used in the following experiments a current of air of constant temperature is sucked with constant velocity over the water surface, and the evaporated water is absorbed and weighed. The arrangement is shown diagrammatically in Fig. 1.

After having passed a drying apparatus, consisting of a bubbler with concentrated sulphuric acid, a drying tower with sodalime, and one with calcium chloride, the air comes to the flowmeter A, which serves for controlling the constant velocity of the air current. The tube *ab* is a capillary, which the air has to pass. The velocity of the flow of air is determined by the pressure difference at *a* and *b*, which can be read on the manometer *c*, filled with coloured olive oil. Then the air goes through the glass spiral B, in order to obtain the same temperature as that of the thermostat, before it enters the wide glass tube C.—As the whole apparatus with the drying towers and the flowmeter was inside a large air thermostat, the current of air has the same temperature as the thermostat.—In the tube C there are some sheets of metal gauze in order to make the air flow uniformly through the whole section of the wide tube. Then there is on a metal stand the crystallizing dish *d*, containing the water with the oil film on its surface.

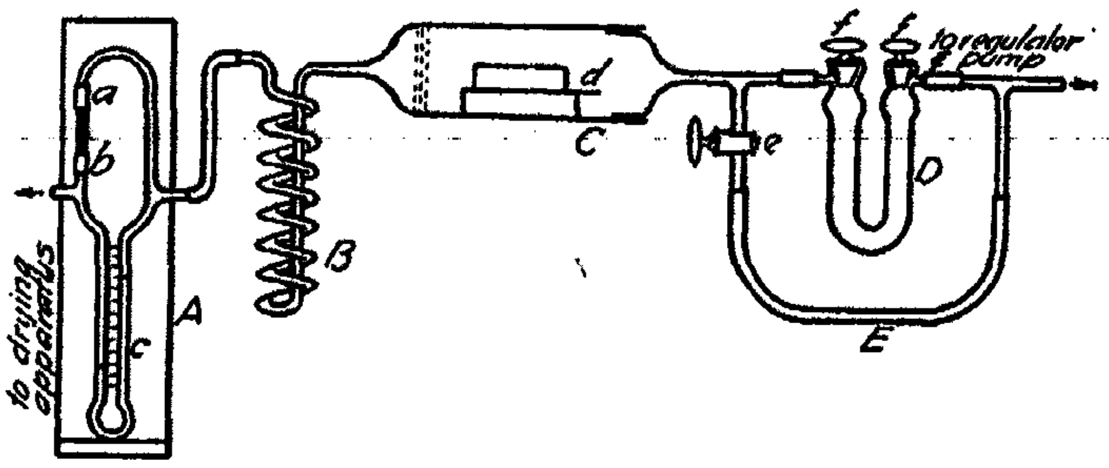

Fig. 1

As the amount of water vapour carried away with the air current varied largely with the height of the edge of the vessel above the water surface, it was necessary in all experiments to have the surface at the same height. This was attained by pouring always with a pipette the same amount of water into the vessel. The water surface was about 0.4 mm. below the edge of the vessel, whose cross-section was 18.2 sq. cm.

The right end of the tube C is closed by a well-fitting ground joint. Great care was taken in putting in the dish and closing the tube that the water did not wet the sides of the dish *d*.

The evaporated water is carried away by the flowing air and absorbed in the U-tube D, filled with dehydrated calcium chloride. When a high speed of the current of air was used, two absorption tubes were put in series. Before the beginning of an experiment, air is sucked through the apparatus past the absorption tube through the rubber tube E, to let the water in the little vessel obtain the temperature of the thermostat. This way for the air current could be closed with the tap *e*, and then the absorption tube was brought in by opening the taps *ff*.

The current of air was obtained by sucking with a filter pump, but as the fluctuations of such a pump are rather large, it was necessary to regulate the flow of air with a self-working regulator. Such a regulator was readily obtained by using the principle of the manostat described by Arndt[1] in his hand-book. In this way it was possible to maintain the current so constant that the height of the oil column of the manometer did not vary more than ±0.2 mm.

The reproducibility of the method proved to be good, the limits of error being less than 1 per cent.

2. Theoretical Remarks

However, there are some theoretical objections that may be considered here. As the evaporation occurs in air of atmospheric pressure, the measured rate is not the real rate of evaporation, but in addition there is a diffusion effect. On the surface of the water in the vessel (Fig. 2.) there is the unimolecular layer *a* of oil, that the evaporating molecules have first to pass through. Above this film there is a stagnant layer *b* of air, through which water molecules diffuse, before they are carried away by the flowing air.

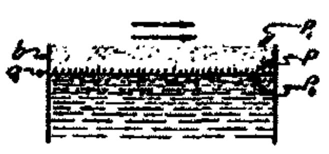

FIG. 2

Let us denote by p_o the vapour tension of water at the temperature used, by p the immediate pressure of water vapour above the oil film, when vapour is constantly flowing away (the *equilibrium* pressure is equal to p_o), and by p_1 the vapour pressure above the stagnant layer of air, that is the pressure of the water vapour in the flowing air. The rate at which the water molecules escape through the oil film is according to the theory of evaporation given by Langmuir[2], determined by the number of water molecules in the surface having an outward velocity high enough to escape the attractive forces of the surface molecules and to overcome the resistance in the oil film; that is, the rate is determined by the vapour tension p_o and the resistance of the oil film.

The rate of diffusion through the adhering layer of air is proportional to the difference p-p_1. Thus, if the current of dry air is so rapid as to carry away all the water molecules coming out from the diffusion layer, p_1 is equal to zero, and the rate of diffusion will be proportional to p, the pressure of water vapour immediately above the oil film, when there is a flow of water vapour away from the film by diffusion. Futher, the rate at which the vapour diffuses, is inversely proportional to the resistance of the stagnant air. The smallest of these two rates, escape through the oil film and diffusion through the adhering air, will be the rate determined by this method.

It seems natural and is à priori probable that the real rate of evaporation of water should be diminished by oil molecules on the surface, and it might

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[1] K. Arndt: "Handbuch phys.-Chem. Technik." (1923).

[2] Phys. Rev. 8, 149 (1916); J. Am. Chem. Soc. 38, 2221 (1916).

be expected that the real rate of evaporation should vary with the number of oil molecules per sq. cm. of the surface as the curve I of Fig. 3 indicates.

In the method used here the measured rate of evaporation will always be proportional to p, the vapour pressure immediately above the oil film, as the rate of diffusion is determined by this pressure. When only little oily substance is spread on the water surface, the resistance of the film will be so small that the equilibrium pressure will be immediately established above the film; in other words, p will be equal to p_0, and the rate of evaporation will remain the same. However, by addition of more and more oil to the surface the resistance of the oil film will increase, and from a certain number of oil molecules per sq. cm. it will become so great that the pressure p will become less than p_0. In consequence the diffusion will be more slow, and the rate of evaporation will fall. The curve we should expect to obtain must therefore be of the shape of curve II in Fig. 3.

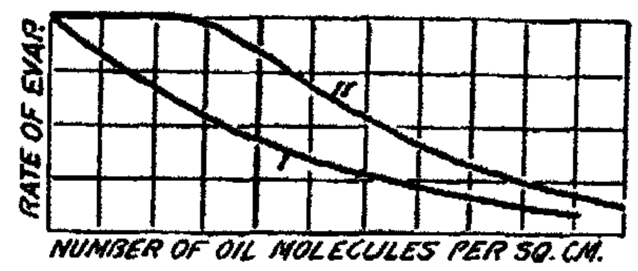

Fig. 3

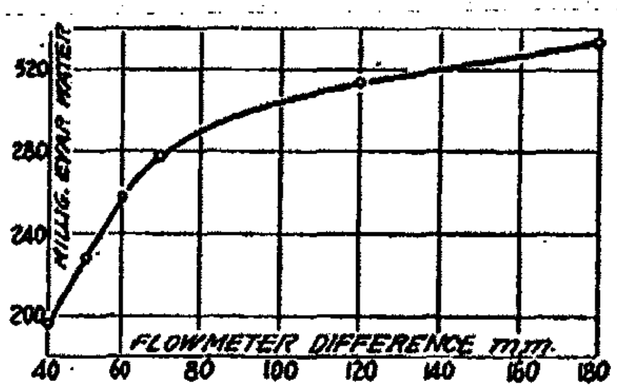

Fig. 4

3. Experimental Results

The apparatus was first calibrated by determining the amount of water evaporated from the clean surface. These values are recorded in Table I and the curve of Fig. 4. In order to show the degree of accuracy of the method the mean errors of the determinations are added. The temperature of the thermostat in these as in all the following experiments was 20°C.

Table I

Diff. on the meter mm.	Evap. water per hour. (milligrams)	Mean error %
40	195.7	0.6
50	227.6	.3
60	257.5	.2
70	277.6	.8
120	312.2	.2
180	331.5	.1

As can be seen from the curve, a velocity of the air current corresponding to the flowmeter difference 180 mm. gives nearly the limiting value of the evaporation.

Table II contains the values obtained when the surface was covered with a film of palmitic acid. The films were deposited on the water in the same way as that used by Adam in his experiments. Pure palmitic acid was dissolved in pure thiophene-free benzene, the solution was appropriately diluted and a counted number of drops was put on the surface with a dropping pipette. The benzene readily spreads and evaporates in a few seconds, leaving a film of the fatty acid behind.

TABLE II

Films of palmitic acid. Flowm. diff. 60 mm.

$\frac{n}{n_1}$	$\frac{m}{m_0}$
0	1.000
0.21	1.001
0.52	1.006
0.94	0.993
1.02	0.991
1.10*	1.000
2.06*	0.990

*After the evaporation of the benzene a small island of "visible" palmitic acid was left on the surface.

The letters of the table have the following meaning: n/n_1 is the ratio between the number (n) of oil molecules on the water surface in the experiment and the number (n_1) required for the formation of a unimolecular, uncompressed film, the area of which is equal to the cross-section (18.2 sq. cm.) of the vessel used. In calculating the number n_1 the value 21.0×10^{-16} sq. cm., obtained by Adam for the cross-section of the hydrocarbon chain, was used. m/m_0 is the ratio between the amount of water evaporated from the oil-covered surface, and that from the clean surface (Table I).

It appears from Table II that the rate of evaporation is not diminished by even the compressed unimolecular film of palmitic acid. A film of equal thickness, more than one molecule deep, cannot be obtained, as the benzene solution does not spread after the unimolecular film has been formed. When more solution is added, a little lens of solution is formed, which evaporates slowly, leaving behind a small lump of solid palmitic acid. Even when only one drop of a stronger solution, containing more acid than corresponding to unimolecular film, is used, it is not possible to obtain films more than one molecule thick, for only part of the drop spreads, the rest forming a lens on the water surface. This fact explains why the amounts of evaporated water are equal for $n/n_1 > 1$. The oil films in these cases are all unimolecular, except at that very small spot, where the solid little lump of acid, many thousand molecules thick, is situated. Of course the films will be more heavily compressed as the amount of benzene solution put on the surface is increased. However, as the coefficient of compressibility of the oil film is small (less than 3 per cent),[1] the amount of fatty acid taken up by the water surface by the compression of the film, is only small.

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[1] N. K. Adam: loc. cit.

Similar results were obtained, when the surface was covered with oleic acid (Table III): no change of the rate of evaporation could be found. Again it was impossible to get films of equal thickness more than one molecule thick, a surplus of the oleic acid collecting to a small globule of pure acid. The latter is in agreement with observations made by Rayleigh[1], Labrouste,[2] and others.

TABLE III

Films of oleic acid. Temp. 20°. Flowmeter difference 60 mm.

$\frac{n}{n_1}$	$\frac{m}{m_0}$
0	1
0.46	1.007
0.92*	1.007
2.30*	0.998
23.0*	1.006

* A small globule of oleic acid was left on the water surface. As oleic acid gives expanded films, a smaller amount of this acid than of palmitic acid, which gives condensed films, is required to build up a unimolecular layer.

In order to see whether the speed of the current of air was too small to let the expected decreasing effect of the oil film on the rate of evaporation appear, some determinations with palmitic acid were made, when a higher speed, corresponding to a flowmeter difference of 180 mm., was used. As pointed out before, this gives almost the "limiting" evaporation. However, the result was the same: no change of the rate of evaporation was obtained, as Table IV shows.

TABLE IV

Films of palmitic acid. Temp. 20°. Flowmeter difference 180 mm.

$\frac{n}{n_1}$	$\frac{m}{m_0}$
0	1
1.05	1.001

As we have seen, the rate of evaporation, as measured by this method, is determined by the vapour pressure immediately above the oil film (at the bottom of the diffusion layer). Connecting this with the results obtained, we can conclude that the vapour pressure above the film very rapidly becomes the same as that above the clean surface. Thus, the evaporation is so rapid, or the resistance of the oil film is so small, that the equilibrium vapour pressure is immediately established above the film, although vapour is continually removed. It therefore seems probable that unimolecular films of fatty acids, even when compressed, only very slightly, if at all, decrease the real rate of evaporation of water.

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[1] Rayleigh: loc. cit.

[2] Labrouste: Ann. Phys. 14, 164 (1920).

Saponin Solutions

Substances such as saponin, which in solution lower the surface tension, concentrate at the surface according to Gibbs' formula, $q = -\frac{C}{RT}\frac{d\gamma}{dC}$, where q is the excess surface concentration. Consequently, in a saponin solution the concentration at the surface is greater than in the bulk of the solution, that is, there must exist an adsorbed layer of saponin molecules at the inside of the surface of the solution. It was of interest to see whether such films, formed by adsorption of a dissolved substance at the water surface, have any effect or not on the rate of evaporation. As the molecular weight of saponin is very great, a solution of not too high a concentration has practically the same vapour tension as pure water. A possible change of the rate of evaporation must therefore be due to the adsorbed surface film.

The results of some determinations on saponin solutions of concentrations up to 2 per cent are given in Table V.

TABLE V

Temp. 20°. Flowmeter difference 180 mm.

Conc. of saponin. %	$\frac{m}{m_0}$
0	1
0.2	1.00
0.5	1.00
1.0	0.99
2.0	1.00

In this table m/m_0 denotes the ratio between the amount of water evaporated from the solution, and that from pure water. These amounts are, within the limits of error, equal, which proves that the rate of evaporation is not influenced by the adsorbed surface film of saponin molecules.

Salt Solutions

According to the values given above, a change of the surface tension seems to have no effect on the rate of evaporation of water. This was supported by some determinations on aqueous solutions of potassium chloride, which increases, and of potassium bromide, which lowers the surface tension of water. The concentrations were chosen so that the two solutions had equal vapour pressures.

TABLE VI

2.012 N. Potassium chloride. Surface tension 1.04 (Water = 1).

Flowmeter diff. mm	$\frac{m}{m_0}$	$\frac{p}{p_0}$
120	0.025	0.924
180	0.925	

TABLE VII

2 N Potassium bromide. Surface tension 0.93 (Water = 1)

Flowmeter diff. mm	$\frac{m}{m_0}$	$\frac{p}{p_0}$
60	0.930	
120	0.915	0.924
180	0.923	

From the Tables VI and VII it is evident that, within the accuracy of the method, the rate of evaporation is equal for the two solutions. Thus, a possible change, if any, of the rate of evaporation, caused by a change of the surface tension, is so small that it is completely covered by the diffusion effect. A comparison of the values of m/m_0 with those of p/p_0, the quotient between the vapour pressure of the solution and that of pure water, shows that the rate of evaporation is proportional to the vapour tension.

As the vapour tension of water is not changed by a thin oil film, the results obtained with salt solutions support the conclusion that the decrease in the rate of evaporation of water, caused by a unimolecular film of fatty acids, is very small, if any at all. Indeed, this fact too is in favour of the conception that the relation between the water molecules in the surface and the oil molecules is a very intimate one. Thus, we cannot regard an oil film *merely* as a thin layer of oil floating on the water, though it behaves in many respects as if it were so, but we must consider the oil molecules as adsorbed, that is according to Langmuir,[1] chemically bound by the electric stray fields of the surface molecules and partly "dissolved" in the water. They are, therefore, forced to follow the thermal agitation of the water molecules, the result of which is a definite evaporation. In this way we can understand that an oil film does not oppose any considerable "resistance" to the escaping water molecules and that the rate of evaporation is not diminished. The same reasoning can be applied to the case of a surface film, formed by the adsorption of a substance in solution.

I wish to express my best thanks to Professor Donnan, for the great interest he has taken in the progress of this work and for his valuable suggestions.

Physico-Chemical Laboratory,
University College, London.
December, 1923.

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[1] Langmuir: J. Am. Chem. Soc. 39, 1848 (1917).

ADSORPTION BY PRECIPITATES VII

BY HARRY B. WEISER

The Influence of Non-Electrolytes on the Precipitation of Sols by Electrolytes

Thirty years ago Bodländer[1] found that small amounts of electrolytes caused rapid clarification of kaolin suspensions, whereas soluble non-electrolytes appeared to have no effect even when added in large quantities. The latter observation has been disproven by the recent investigations of Rona and György[2] using a large variety of non-electrolytes such as diphenylthiocarbamid, chloroform, tributyrin, camphor, thymol, a number of alcohols, and urethanes. The presence of every compound except those that are virtually insoluble in water, was found to increase the velocity of kaolin sedimentation. Since the effect of the non-electrolytes could not be due to the slight change in the viscosity of the medium, Rona and György concluded that the compounds added, produced a sensitization of the suspended particles toward the electrolytes always present and thus increased the velocity of sedimentation.

Such a sensitization of colloids by non-electrolytes has been observed by a number of investigators. Thus Billitzer[3] found that a negatively charged platinum sol could be sensitized, discharged, or even changed into a negative sol by the addition of suitable amounts of alcohol; Wo. Ostwald[4] precipitated a silver sol with propyl alcohol; and Klein[5] showed that negatively charged sols of arsenious sulphide, gold, silica, and ferric oxide were agglomerated in part by alcohols; whereas positively charged ferric oxide and silica were not. Freundlich and Rona[6] observed that the addition of camphor, thymol, and urethanes to ferric oxide sol reduced the precipitation concentration of electrolytes. For example, the precipitation value of sodium chloride in the absence of non-electrolytes was 35 millimols per liter. This value was decreased to 27 in the presence of 10 millimols per liter of camphor; and to 20 in the presence of 5 millimols per liter of thymol.

The sensitization of sols by non-electrolytes has been attributed by Wo. Ostwald[7] and Cassuto[8] to a change in the dielectric constant of the medium. Freundlich[9] suggests that the sensitization results from the lowering of the charge on the particles by adsorption on their surface of the organic non-

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[1] Jahrbuch Min., 2, 147 (1893).

[2] Biochem. Z., 105, 133 (1920); cf. Quincke: Drude's Ann., 7, 57 (1902).

[3] Z. physik. Chem., 45, 312 (1903).

[4] "Grundriss der Kolloidchemie", 471 (1909).

[5] Kolloid-Z., 29, 247 (1921).

[6] Biochem. Z., 81, 87 (1917).

[7] Loc. cit.

[8] "Der kolloide Zustand der Materie", 152 (1923).

[9] "Kapillarchemie", 637 (1922).

conductor which has a dielectric constant appreciably lower than that of water. It has been shown that the charge, e, on a single colloidal particle,

$$e = \frac{\mathrm{E\,Dr\,(r+d)}}{\mathrm{d}}$$

where E is the potential difference of the double layer at the surface of a spherical particle of radius r, D is the dielectric constant and d the thickness of the double layer. From this it follows that the lower the dielectric constant the lower the charge on a particle. This would mean that the amount of a precipitating ion that must be adsorbed to effect neutralization will be less and so the precipitation value of an electrolyte will be decreased as Freundlich observed with ferric oxide sol. Furthermore, as the velocity of migration, u, of a colloidal particle in an electric field is given by the expression:

$$\mathrm{u} = \frac{\mathrm{E\,H\,D}}{4\,\pi\,\eta},$$

a decrease in D will cause a falling off in u. That such is the case was demonstrated by Freundlich and Rona who found for a pure ferric oxide sol, $\mathrm{u} = 0.4 \times 10^{-4}$ cm/sec for a potential of one volt/cm, while for a sol containing 5 millimols of camphor per liter, $\mathrm{u} = 0.2 \times 10^{-4}$ cm/sec and for one containing 25 millimols thymol per liter $\mathrm{u} = 0.3 \times 10^{-4}$ cm/sec. From the slope of the adsorption isotherms, Freundlich also deduced that the decrease in precipitation value will be appreciable only for electrolytes containing univalent precipitating ions that are weakly adsorbed; and will be very slight or negligible for electrolytes containing strongly adsorbed precipitating ions.

From conclusions drawn by Freundlich as a result of his investigations on ferric oxide sol, it would appear to follow that the addition to colloids of non-electrolytes having a lower dielectric constant than water, will always decrease the precipitation value of electrolytes; and that this effect will be greater the lower the dielectric constant of the non-conductor added. These deductions appear to be disproven by the investigations of Kruyt and van Duin[1] on arsenious sulphide sol. They found that the effect of non-electrolytes such as phenol and isoamyl alcohol on the precipitation value of electrolytes was determined by the nature of the precipitating ion; for univalent and trivalent ions the precipitation value was lowered; while with bivalent and tetravalent ions it was raised. Moreover, for any given electrolyte the change in the precipitation value seemed to be independent of the dielectric constant of the non-electrolytes employed. Kruyt and van Duin[2] studied the adsorption of non-electrolytes by charcoal and found for a given electrolyte, that there was a parallelism between the effect of different non-electrolytes on the precipitation value for colloidal arsenious sulphide and the adsorption of the non-electrolytes by carbon. However, they were unable to account for the fact that the same non-electrolyte appears to stabilize a

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[1] Kolloidchem. Beihefte, 5, 1270 (1914).

[2] Cf. van Duin: Kolloid-Z., 17, 123 (1915).

sol toward certain electrolytes and to sensitize it toward others. The experiments to be recorded in the next section throw some light on the mechanism of the process which accounts for these apparent anomalies.

Experiments with Colloidal Arsenious Sulphide

For a satisfactory study of adsorption during the precipitation of sols, the latter must not be too dilute, otherwise the change in concentration of electrolyte due to adsorption, will be insufficient to measure accurately. As Kruyt and van Duin did not give the concentration of the sol they employed, it was necessary, at the outset, to determine the effect of concentration of sol on the precipitation value of an electrolyte in the presence of a constant amount of non-electrolyte. The initial experiments were made with colloidal arsenious sulphide prepared by dropping a solution of arsenious oxide into water through which was bubbled a stream of carefully washed hydrogen sulphide. The sol was washed free from hydrogen sulphide by hydrogen and kept in an atmosphere of the latter gas.

Precipitation experiments. The concentration of the original sol used in these experiments was 12.5 gms. per liter. From this, more dilute sols were prepared and the precipitation value of electrolytes was determined for each, both in the presence and absence of phenol. The procedure was as follows: After determining the approximate precipitation value, 10 cc. of colloid was diluted in a test tube with 5 cc. of water or 5 cc. of phenol solution and allowed to stand 20 minutes. This was then placed in the outer compartment of a small mixing apparatus similar to that employed in earlier experiments.[1] In the inner compartment was placed a definite amount of electrolyte diluted to 5 cc. The electrolyte was measured with a 2 cc. pipette graduated in 0.05 cc. After mixing, the contents were poured into the test tube that held the colloid originally and the mixture allowed to stand 2.5 hours, shaking at the end of the one- and two-hour intervals. To determine whether or not precipitation was complete, the contents of the test tube were centrifuged

TABLE I

Precipitation of Colloidal Arsenious Sulphide

Concentration of colloid	Precipitation Values Milliequivalents per liter			
	without phenol		with phenol*	
	KCl	$BaCl_2$	KCl	$BaCl_2$
100% (12.55 g. per 1)	75.6	1.713	44.4	2.288
50%	81.8	1.325	50.6	2.100
25%	83.9	1.440	53.1	2.025
12.5%	86.9	1.400	54.4	2.000

*Concentration of phenol 170 milliequivalents per l.

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[1] Weiser: J. Phys. Chem., 24, 48 (1920).

and a portion of the supernatant liquid examined for the presence or absence of the slight greenish opalescence which serves to detect very minute amounts of the colloidal sulphide. The results with KCl and $BaCl_2$ are given in Table I and are shown graphically in Fig. 1. The concentration of the sols is expressed in percent, taking the most concentrated as 100%. The curves given in Table I were obtained by plotting concentration against ratio of each precipitation value for an electrolyte to that of the strongest colloid. It will be noted that the precipitation value of KCl increases and that of $BaCl_2$ decreases with dilution of the pure sol, a circumstance that has been considered in detail in an earlier paper[1].

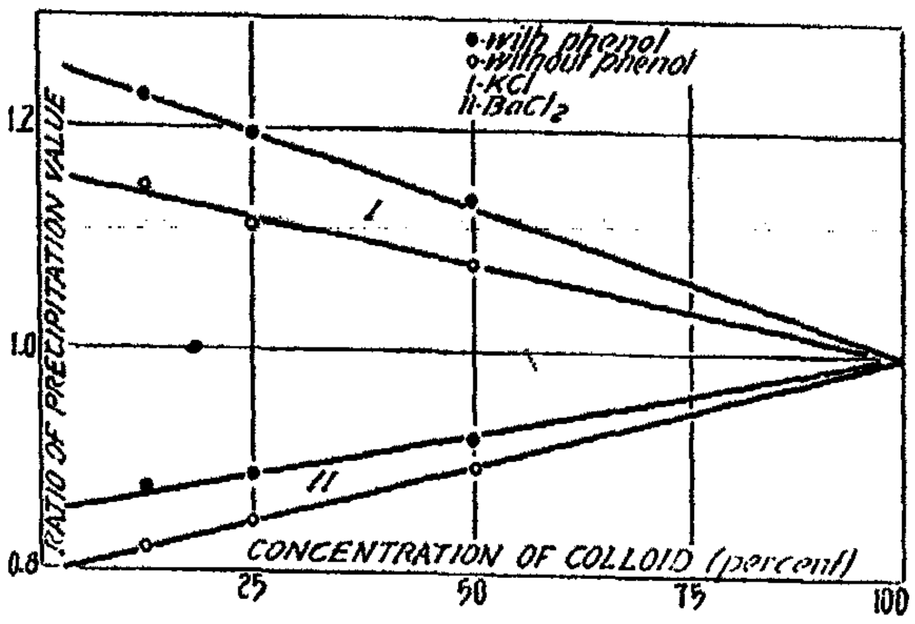

FIG. 1

The presence of phenol lowers the precipitation value of KCl and increases that of $BaCl_2$ for sols of all concentrations between 12.5 gms. and 1.5 gms. As_2S_3 per liter. In both cases the "phenol" curves are slightly above those for the pure sol, showing that the percentage lowering of the precipitation value of KCl in the presence of phenol is relatively greater than the percentage raising of the precipitation value of $BaCl_2$. Since the effect of phenol on the precipitation value is of the same general character with sols of widely varying concentrations, there appeared to be no objection to working with a sol that was sufficiently concentrated to make satisfactory adsorption studies.

If the addition of a non-electrolyte to a sol sensitizes it, one should not expect the precipitation value of $BaCl_2$ to be raised as the observation discloses. In view of this apparent abnormality, and the relative ease with which barium ion may be determined, the following experiments were carried out:

It was necessary, first of all, to determine whether an accurate estimation of barium could be made by precipitation as sulphate in the presence of phenol and of isoamyl alcohol. That this can be done is clear from the results of the experiments recorded in Table II.

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[1] Weiser and Nicholas: J. Phys. Chem., 25, 742 (1921).

TABLE II
Standardization of Barium Chloride

Contents of solution analyzed				
$BaCl_2$ approx. N/50 cc	Non-electrolyte cc		Water cc	Weight of $BaSO_4$
	Phenol 66.0 g/l	Isoamyl alcohol 17.0 g/l		
50	....	....	100	0.1162
50	....	....	100	0.1163
50	50	....	50	0.1158
50	....	50	50	0.1162

The arsenious sulphide sol used in the following experiment was prepared as previously described; it contained 31.3 gms. As_2S_3 per liter. The precipitation value of $BaCl_2$ was determined both in the absence and in the presence of phenol and of isoamyl alcohol. For the purpose of the experiments to be described later on, the precipitation value with mixtures of $BaCl_2$ and $AlCl_3$ in the presence of phenol, were also determined. In accord with earlier observations, the precipitating action of such mixtures is approximately additive[1]. All values are given in cubic centimeters of solution employed. The solutions of non-electrolytes used, were approximately saturated at ordinary temperatures. The effects are therefore the maximum that could be obtained by the procedure employed.

TABLE III
Precipitation of Colloidal Arsenious Sulphide

	Solutions mixed that effect precipitation Total volume 20 cc.				
No.	Colloid 31.3 g per 1	Phenol 66.0 g per 1	$BaCl_2$ N/50	$AlCl_3$ N/100	H_2O
I	10	0	3.14	...	6.86
II	10	5	4.23	...	0.77
	10	5	...	1.51	3.49
III	10	5	3.14	0.36	1.50
IV	10	5	2.00	0.83	2.17
V	10	5	1.00	1.18	2.82
		Isoamyl alcohol 17.0 g. per 1			
VI	10	5	3.94	...	1.06
VII	10	5	3.14	0.25	1.61

Adsorption Experiments. Adsorption experiments were carried out in the following manner: To 100 cc. of colloid was added 50 cc. of water or non-electrolyte and the mixture placed in the outer compartment of a mixing

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[1] Weiser: J. Phys. Chem., **25**, 665 (1921); **28**, 232 (1924).

apparatus of suitable dimenions. In the inner compartment was placed the required amount of electrolyte diluted to 50 cc. After standing 20 minutes the contents of the apparatus were shaken thoroughly and then transferred to a 250 cc. bottle. After standing 2½ hours the precipitate was matted in the bottom of the vessel by the aid of a centrifuge and a definite volume pipetted off for analysis. Since the solution usually contained a minute trace of sulphide, it was allowed to stand 24 hours and was then filtered through a small filter paper. The subsequent analysis was carried out as nearly as possible under the same conditions as were used in standardizing the solution. The results of a series of seven experiments (corresponding in number to those in Table III) are recorded in Table IV and shown graphically in Figure 2.

TABLE IV

Adsorption of Barium Ion by Arsenious Sulphide

Solutions mixed with 100 cc. colloid contg. 31.5 g. As_2S_3				$BaSO_4$ remaining in 180 cc.		Barium adsorbed Grams per mole As_2S_3
No.	N/50 $BaCl_2$ cc	Phenol cc	H_2O cc		Average	
I	31.40	0	68.60	0.0501		
	31.40	0	68.60	0.0503	0.0502	0.805
II	42.35	50	7.65	0.0749		
	42.35	50	7.65	0.0753	0.0751	0.708
III	31.40	50	15.00[1]	0.0531		
	31.40	50	15.00[1]	0.0530	0.0531	0.657
IV	20.00	50	21.70[2]	0.0312		
	20.00	50	21.70[2]	0.0315	0.0314	0.538
V	10.00	50	28.20[3]	0.0132		
	10.00	50	28.20[3]	0.0136	0.0134	0.381
		Isoamyl alcohol				
VI	39.36	50	10.64	0.0680		
	39.36	50	10.64	0.0679	0.0680	0.753
VII	31.40	50	16.10[4]	0.0519		
	31.40	50	16.10[4]	0.0521	0.0520	0.713

[1] + 3.60 cc. N/100 $AlCl_3$.
[2] + 8.30 cc. N/100 $AlCl_3$.
[3] + 11.80 cc. N/100 $AlCl_3$.
[4] + 2.50 cc. N/100 $AlCl_3$.

The results recorded in Table IV are so significant that but little comment is necessary. Comparing the results of experiment I with those of experiment II, it will be observed that the adsorption is less in the presence of phenol although the amount of electrolyte that must be added to effect precipitation is greater. This means that the sol is sensitized, in the sense that less barium ion must be adsorbed in order to lower the charge on the particles below the critical value necessary for agglomeration and precipitation. The fact that a higher concentration of barium must be present to cause precipitation of the sensitized sol is due to the marked influence of the adsorption of phenol on the adsorption of barium ion. This is demonstrated clearly in experiment III in which the adsorption of barium in the presence of phenol is determined at the concentration of electrolyte that will cause precipitation in the absence of phenol. It will be noted that the adsorption is cut down almost 20%. This cutting down of the adsorption is not due to the very low concentration of aluminum ion (0.0018 N) since there is very little if any antagonistic action under these conditions. Similar results were obtained with isoamyl alcohol as shown by experiments VI and VII.

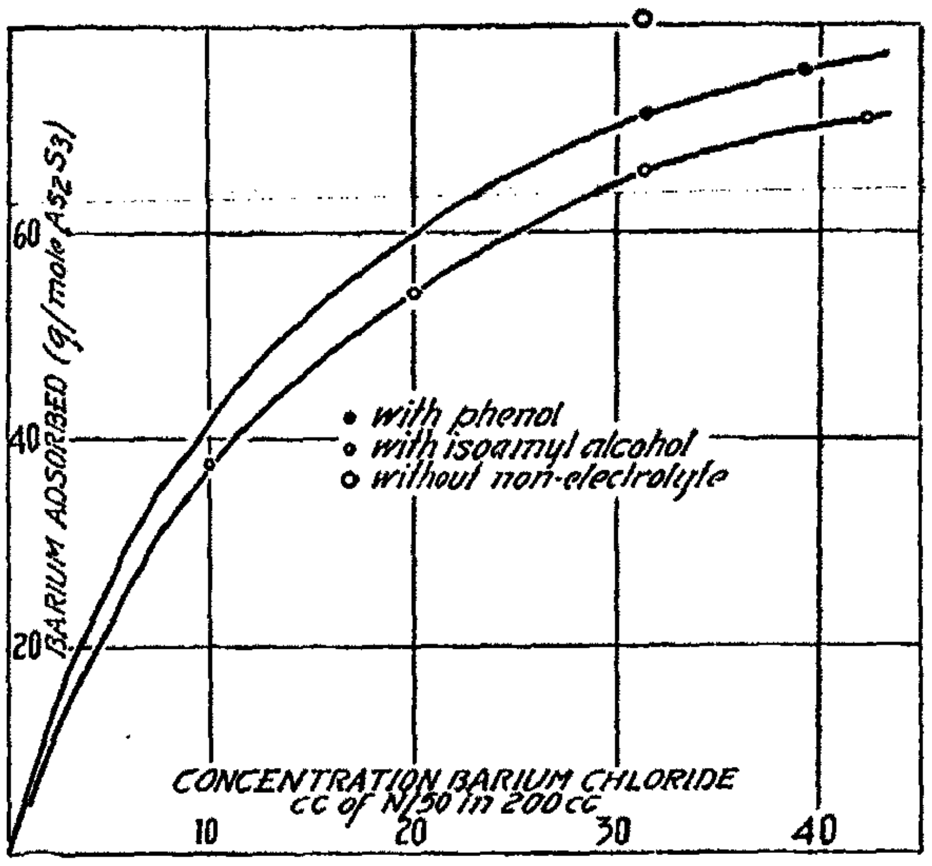

Fig. 1

Comparing experiment III with VII, it will be noted that the adsorption of barium at the precipitation value of $BaCl_2$ in the presence of phenol is less than that in the presence of isoamyl alcohol. This indicates that phenol has sensitized the sol more than the alcohol, a result that might be expected from a comparison of the dielectric constants of the two compounds. It should be pointed out however, that the concentration of phenol is higher than that of the alcohol. Moreover we have no measure of the relative adsorbability of the two non-electrolytes by the colloidal particles. One compound that is strongly adsorbed may have a greater effect than the same concentration of another compound having a higher dielectric constant, that is less strongly adsorbed.

Attention should be called to Figure 2 which shows that the adsorption of barium *below* the precipitation concentration follows the well-known adsorption isotherm. Such a result was predicted by Freundlich and was indicated by some earlier observations made in this laboratory[1]. The truth of this important assumption is now definitely established by direct experimental observation.

As already recorded the precipitation value of KCl is lowered quite appreciably by the presence of phenol. As Freundlich pointed out[2] this is probably due to the relatively flat character of the adsorption isotherm for univalent precipitating ions. With such ions the change in adsorption is usually very slight for relatively large changes in concentration; conversely a slight decrease in the adsorption necessary for lowering the charge on the particles below the critical value will be marked by an appreciable lowering of the precipitation value. Thus a lowering of 10% in the amount that must be adsorbed, such as observed in the preceding experiment, may cause a lowering in the precipitation value of 50% or more, if no other factor enters in. As a matter of fact, the presence of phenol doubtless cuts down the adsorption of potassium ion[3], a circumstance that would tend to increase the precipitation value. This effect is of course much less marked than in the case of $BaCl_2$ since the concentration of potassium ion is approximately 100 times greater than that of barium ion. Moreover, the high precipitation value of KCl results, in part, from the fact that the adsorption of chloride ion at certain concentrations, is comparable to that of potassium ion[4]. Since the presence of phenol doubtless cuts down the adsorption of chloride ion as much or more than that of potassium ion, this amounts to a sensitization of the sol and a consequent descrease in the precipitation value. With $BaCl_2$ as precipitant, the concentration of the relatively slightly adsorbed chloride ion at the precipitation value is too low to have any appreciable influence.

We may now consider what will be the influence of a like amount of phenol or isoamyl alcohol on the precipitation value of a salt with a trivalent precipitating ion such as $AlCl_3$. On account of the steep slope of the adsorption isotherm for aluminum ion as compared with that of a univalent ion, one should expect the small sensitization of the sol to lower the precipitation value but slightly[5]. Opposing this, is the cutting down of the adsorption of

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[1] Weiser: J. Phys. Chem., 28, 232 (1924).

[2] "Kapillarchemie", 638 (1922).

[3] According to Lachs and Michaelis (Kolloid-Z., 9, 275 (1911), the adsorption of chloride ion from solution by charcoal is not changed appreciably by the presence of phenol or isoamyl alcohol. On account of the high precipitation value of potassium chloride and the relatively small change in concentration of potassium ion after precipitation of arsenious sulphide sol, it was impossible to determine accurately the adsorption of potassium ion in the presence and the absence of non-electrolytes.

[4] Cf. Weiser: J. Phys. Chem., 25, 680 (1921); 28, 241 (1924).

[5] Cf. Freundlich: Loc. cit.

aluminum ion by adsorbed non-electrolyte. This latter effect should also be small on account of the very strong adsorption of aluminum ion even in low concentration. The sum of these two opposing influences would be expected to give a net change in the precipitation value that is very slight or negligible. Kruyt and van Duin claimed, however, that the precipitation value of $KAl(SO_4)_2$ is lowered quite appreciably by the presence of phenol or isoamyl alcohol. It is impossible to say how this result was obtained; but we have been unable to confirm it by repeated observations on several different sols and on several concentrations of the same sol. A few of these observations are given in Table V. For the more concentrated sols the difference in precipitation value is too small to be detected. With very dilute sols the precipitation value appears to be slightly greater rather than less in the presence of phenol. Since the concentration of aluminum ion necessary for precipitation is so low and the adsorption so great, the amount that remains in solution after precipitation is, unfortunately, too small to detect the very slight difference in adsorption that must exist in the presence and the absence of non-electrolytes.

TABLE V

Precipitation of Colloidal Arsenious Sulphide with Aluminum Salts

Electrolyte	Concentration of colloid g per l	Concentration of phenol; milli-equivalents per l	Precipitation values milliequivalents per l	
			without phenol	with phenol
$AlCl_3$	31.50	170	0.075	0.075
$AlCl_3$	6.17	170	0.025	0.025
$AlCl_3$	34.70	158	0.063	0.063
$AlCl_3$	0.385	170	0.012	0.013
$KAl(SO_4)_2$	13.43	170	0.048	0.048
$KAl(SO_4)_2$	34.70	158	0.081	0.081
$KAl(SO_4)_2$	1.10*	170	0.013	0.014

* Sol. prepared by the method of Freundlich and Nathanson: Kolloid-Z., 28, 258 (1921).

Experiments with Colloidal Hydrous Oxides

Precipitation Experiments. Colloidal hydrous ferric oxide and hydrous chromic oxide were prepared by Neidle's method[1] and dialyzed in the hot for several days. The precipitation concentrations of various electrolytes with and without the presence of phenol and isoamyl alcohol were determined as previously described for arsenious sulphide, except that the solutions after mixing were allowed to stand quietly for 2½ hours after which they were centrifuged to determine whether precipitation was complete. The results which are recorded in Table VI, indicate that the hydrous oxide sols

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[1] J. Am. Chem. Soc., 39, 71 (1907).

are sensitized but slightly by the presence of phenol or isoamyl alcohol. The precipitation concentration of KCl is lowered a small amount by the presence of a non-electrolyte while that of salts with multivalent precipitating ions is changed but little if at all. These results are in agreement with those of Freundlich on hydrous ferric oxide to which reference has already been made. From these observations we should expect phenol and isoamyl alcohol to have little influence on the adsorption of multivalent ions during the precipitation of the colloidal oxides.

TABLE VI

Precipitation of Colloidal Hydrous Oxides

Colloid	Electrolyte	Precipitation value milliequivalents per liter.		
		without non-electrolyte	with phenol	with isoamyl alcohol
Fe_2O_3	KCl	40.5	37.1	36.2
	$K_2C_2O_4$	0.405	0.405	....
	K_2SO_4	0.433	....	0.424
Cr_2O_3	$K_2C_2O_4$	0.630	0.610	....
	K_2SO_4	0.637	....	0.632

Adsorption Experiments. The adsorption of multivalent precipitating ions by hydrous oxides is so strong that most of them are adsorbed at the precipitation concentrations. Since the critical values are practically the same both in the presence and the absence of non-electrolytes, it is impossible to detect any change in adsorption at this point. Accordingly, some observations were made above the precipitation value of K_2SO_4 using both colloidal ferric oxide and colloidal chromic oxide. The procedure was identical with that described for the adsorption of arsenious sulphide, except that the solutions were not stirred after the initial mixing. The results are given in Tables VII and VIII.

TABLE VII

Adsorption of Sulphate Ion by Hydrous Chromic Oxide

Solutions mixed with 100 cc colloid contg. 0.2 g Cr_2O_3			$BaSO_4$ remaining in 170 cc. gms.		Sulphate adsorbed gms. per mole Cr_2O_3
N/50 K_2SO_4 cc	Non-electrolyte cc	H_2O cc		average	
25	0	75	0.0361		
25	0	75	0.0359	0.0360	5.00
	isoamyl alcohol				
25	50	25	0.0363		
25	50	25	0.0361	0.0362	4.95
	phenol				
25	50	25	0.0361		
25	50	25	0.0361	0.0361	4.96

TABLE VIII

Adsorption of Sulphate Ion by Hydrous Ferric Oxide

Solutions mixed with 100 cc colloid contg. 3.51 g Fe_2O_3			$BaSO_4$ remaining in 175 cc gms.		Sulphate adsorbed gms. per mole Fe_2O_3
N/50 K_2SO_4 cc	non-electrolyte cc	H_2O cc		average	
20	0	80	0.0296		
20	0	80	0.0292	0.0294	2.50
	isoamyl alcohol				
20	50	30	0.0293		
20	50	30	0.0294	0.0293	2.49
	phenol				
20	50	30	0.0289		
20	50	30	0.0293	0.0291	2.45

As was to be expected from the precipitation experiments, the adsorption of sulphate by the hydrous oxides is approximately the same in the presence as in the absence of phenol and isoamyl alcohol. With both sols there appears to be a slight decrease in adsorption in the presence of the non-electrolytes. While this is as it should be, the results are scarcely accurate enough definitely to establish such a tendency.

Summary and Conclusions

1. A study has been made of the adsorption during the precipitation by electrolytes, of negative arsenious sulphide sol and of positive hydrous ferric oxide and hydrous chromic oxide sols both in the presence and the absence of phenol and of isoamyl alcohol.

2. The adsorption of a non-electrolyte by the particles of a sol decreases the stability of the latter, in the sense that less of a precipitating ion must be adsorbed in order to decrease the charge below the critical value necessary for agglomeration and precipitation. The extent of the sensitization depends on the concentration and adsorbability of the non-electrolyte and its dielectric constant. This effect tends to lower the precipitation value of an electrolyte. The amount of the lowering is greatest for electrolytes with weakly adsorbed precipitating ions that precipitate only in relatively high concentration.

3. The adsorption of a non-electrolyte by the particles of a sol cuts down the adsorption of the precipitating ion of the electrolyte added to produce coagulation. This effect tends to raise the precipitation value of an electrolyte.

4. Since the factors given in (2) and (3) have opposite effects on the precipitation value of electrolytes, it follows that, depending on the conditions, the precipitation value may be increased, decreased or remain unchanged in the presence of a non-electrolyte.

5. The adsorption of barium ion by colloidal arsenious sulphide has been determined at a number of concentrations *below* the precipitation value. On plotting the results of these observations, a typical adsorption isotherm was obtained.

I am indebted to Miss Charlotte Schaler, an Honors Student in Chemistry, for preparing the colloidal solutions used in this investigation and for making a number of the precipitation experiments.

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VAPORIZATION OF LIQUID MIXTURES*

BY J. F. KING AND S. P. SMEDLEY

Introduction

Among the different classes of physical mixtures, the simplest ones and the ones for which the relations have been most satisfactorily worked out are the gaseous mixtures. The generalizations of Raoult and van't Hoff along with the work of many investigators such as that of Morse and Frazer have cleared up to a great extent the behavior of mixtures of solids in liquids. In this class the relations are quite well understood, at least, for certain ones of solids in liquids where the mol fraction of solid is small. The properties, however, of mixtures of liquids in liquids are not so well understood and the relations which exist in this class are apt to be quite complicated. Seldom are the properties additive or can they be calculated from the properties of the pure components. We, therefore, can classify all liquids into two groups, those which form ideal mixtures with normal properties and those whose mixtures have abnormal properties.

One of the most important properties of liquid mixtures is that of vapor pressure. This property is made use of whenever it is desired to separate the liquids by fractional distillation. The abnormal liquids give the mixtures which are constant evaporating, having a maximum or minimum vapor pressure. The normal liquids can be separated from their mixtures by fractional distillation. Frequently chemists wish to know whether a given pair of liquids forms a constant evaporating mixture.

The determination of the vapor pressure curve for a series of liquid mixtures gives a method for determining the existance of a constant evaporating mixture. However, once the vapor pressure curve has been constructed, it is usually difficult to determine just what the composition of the mixture is which has the maximum or minimum vapor pressure because of the flatness of the vapor pressure curve. One can use the method of Rosanoff[1] of finding the equation of the curve and solving for the point of inflection. Still this does not enable one to locate the composition of the mixture any more closely. Chemists usually make use of distillation methods for determining the constant evaporating mixture. The distillation method is a tedious one to carry out and quite difficult where the mixture has to be determined with any degree of accuracy. In this paper we give three simple and rapid methods which can be used for determining the composition of the constant evaporating mixture.

First Method

Determination of the Vapor Pressure Curve

Several static and dynamic methods for determining the vapor pressure of mixtures of liquids have been worked out. The principal objection to all these

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*Contribution from the Thompson Chemical Laboratory of Williams College.

[1] J. Am. Chem. Soc. 36, 1993 (1914).

methods is the length of time necessary to complete a determination and the difficulty of manipulation. Chemists appear to favor the dynamic methods.

Among the dynamic methods are:

1. The method of boiling points where the boiling points of a series of liquid mixtures are determined at different pressures. Then the pressures corresponding to a certain temperature are plotted against composition. The objection to this method is the large number of observations needed for the construction of the vapor pressure curve.

2. The air saturation method gives an accurate method for determining the total vapor pressure as well as the partial pressures of the mixtures. The objection to this method is the large amount of time necessary to bring the air to saturation as it is drawn through the mixtures.

3. We also have the method worked out by Rosanoff, Bacon and White[1] of passing a vapor of known composition through the mixture until equilibrium is reached and then analysing the mixture. This method is also slow of operation and difficult of manipulation.

The "submerged bulblet" method of Smith and Menzies[2] gives a very simple, rapid and accurate method for determining vapor pressures and boiling points. This method has been applied to:—

1. The determination of the boiling point of a pure liquid.

2. The determination of the vapor pressure or the sublimation point of a pure solid.

3. The determination of the purity of a liquid by noting the changing boiling point as vaporization takes place.

4. The determination of the vapor pressure curves of pure substances.

From the "submerged bulblet" method, Smith and Menzies developed their "static isotenoscope"[3] and their "dynamic isotenoscope"[4]. Their static isotenoscopic method can be adapted to the determination of the vapor pressures of mixtures of liquids. Here again, however, we find the method rather difficult of manipulation.

It has been our purpose to modify the very simple and rapid "submerged bulblet" method of Smith and Menzies for the determination of the vapor pressure curve of liquid mixtures. The method as worked out by Smith and Menzies cannot be so used because there is no provision for keeping the composition of the surface of the liquid mixture the same as the body of the mixture. If the mixture could be thoroughly stirred, this method could very easily be used. We have used their modified apparatus in determining the vapor pressure curve for a series of mixtures of carbon tetrachloride and ethyl alcohol.

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[1] J. Am. Chem. Soc. 36, 1803 (1914).

[2] J. Am. Chem. Soc. 32, 897, 907 (1910).

[3] J. Am. Chem. Soc. 32, 1412 (1910).

[4] J. Am. Chem. Soc. 32, 1448 (1910).

In Fig. 1 the shape of their bulblet was changed to the shape as seen at "A". The tenth of a degree thermometer holding the bulblet was passed through a larger glass tube at "a" and fastened to it by a piece of rubber tubing at "b". The thermometer was tapped at "c" by a mechanical device which consisted of a sort of cam, "d", attached to the extended shaft of the stirrer of the thermostat, "e". The thermometer was held back by a rubber band at "f" and as the cam hit the thermometer, it rocked back and forth rapidly in its loose fitting in the glass tubing through the rubber stopper, "g". The effect was to stir the liquids in the bulblet up violently from the bottom and maintain a constant composition throughout. The large neck of the bulblet allowed the splash to drain back into the bulblet. "h" is connected with a large suction bottle and "i" is connected to a mercury manometer for recording the pressure on the inside of the apparatus. With all the precautions and corrections suggested by Smith and Menzies, this method is possible of as great accuracy as they obtained for a single liquid.

The ethyl alcohol was prepared by refluxing over lime. Density 20°/4° was 0.789. Merck C. P. carbon tetrachloride was allowed to stand over KOH for 12 hours. It was then distilled and treated with P_2O_5 and again distilled with a Young fractionating column. Density 20°/4° was 1.594. The mixtures were made up in % by volume. Accurate pipettes were used and the measuring was done in a constant temperature room at 20° C.

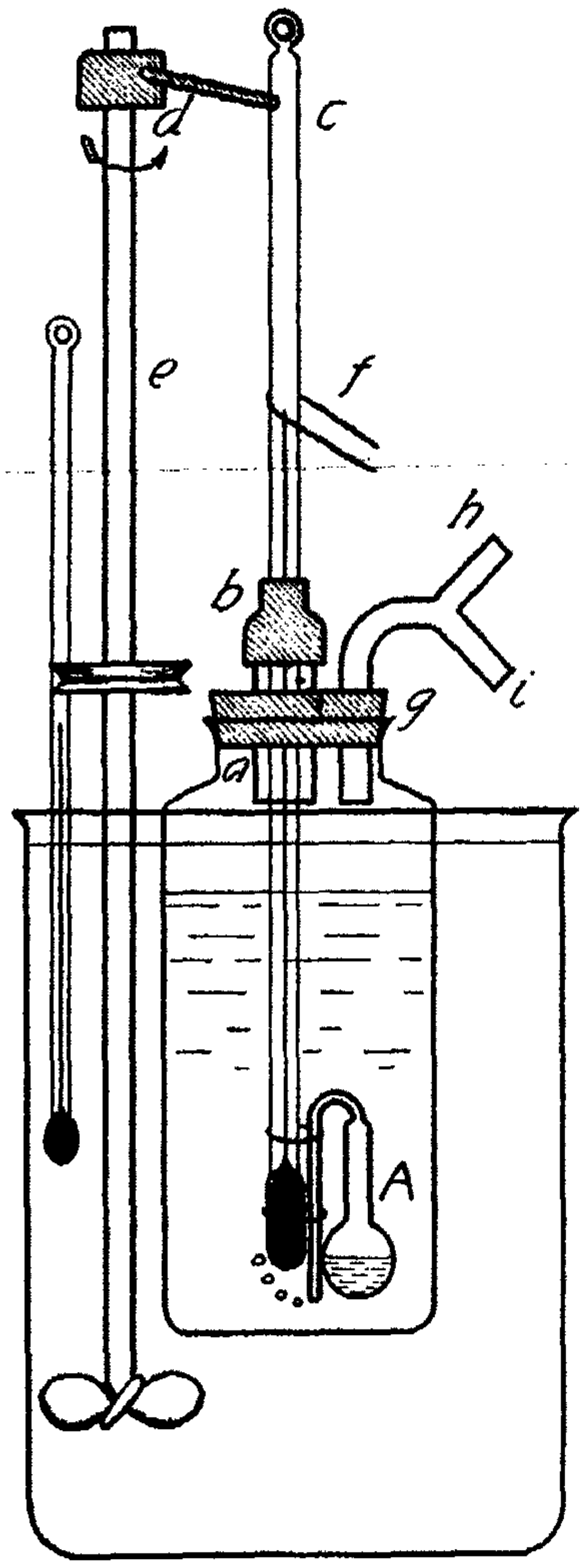

Fig. 1

The bulblets were filled by immersing the ends in the mixtures contained in small flasks. The air was pumped out of the bulblets and the liquid allowed to enter, filling the bulblets half full. The bulblet was fastened to the thermometer by means of rubber bands and the thermometer was fixed in its position in the apparatus. The suction was then applied and after the air in the bulblet had been displaced, a reading, if constant, was taken on the manometer. The vapor pressure was then calculated according to the method of Smith and Menzies. Since we did not care to determine the vapor pressure to an accuracy greater than ± 1 mm., we were able to eliminate some of the finer corrections which they pointed out. Duplicate and triplicate determinations were made. The method is very rapid and simple. The bulblets can all be filled at the start and some eight or ten points determined on the curve in less than two hours. The values which we obtained are as follows:

% alcohol by volume	vapor pressure of mixture at 20°C. mm. Hg.	% alcohol by volume	vapor pressure of mixture at 20°C. mm. Hg.
0	90	50	103
10	111	70	87
20	112	80	75
30	110	90	60
40	108	100	44

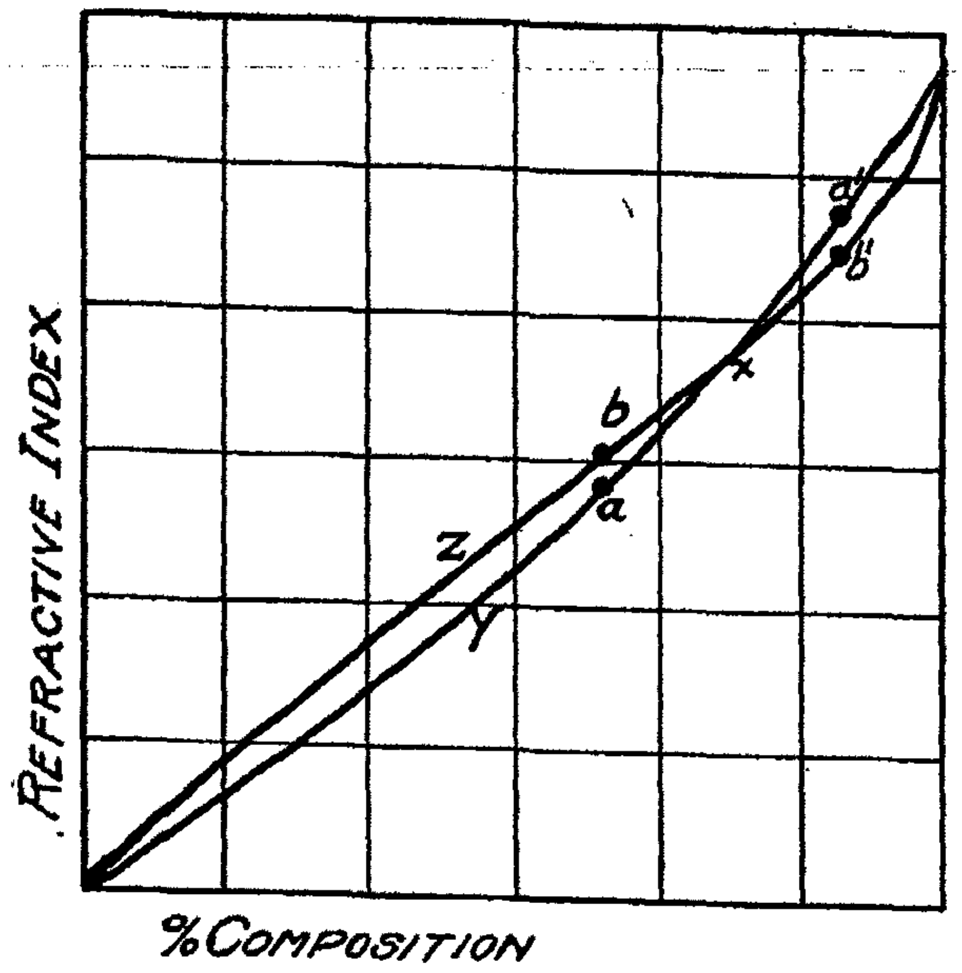

Fig. 2

The Second Method

Determination of the Constant Evaporating Mixture by Use of the Abbe Refractometer

The principle of this method is as follows:—

A series of mixtures of two liquids is made up and the refractive indices of the mixtures are determined by use of the Abbe refractometer. The usual refractive index—composition curve as "y" in Fig. 2 is drawn. Then the prism is opened and a definite amount of one of the mixtures is placed inside and allowed to evaporate for a definite number of seconds. The prism is then closed and the refractive index of the residue is determined. The plotted values give the curve "z" in Fig. 2.

Where the two curves cross at "x" we have a mixture which does not change in composition on evaporation. For an approximate determination of the composition of the constant evaporating mixture, the points "a", "a'", "b", "b'" can be determined. Then since the curves are nearly flat in this region, straight lines can be drawn connecting the points and the point of intersection can be very easily located.

In our determination of the mixture for carbon tetrachloride and alcohol, the prism was kept at 20° by allowing water from a thermostat to circulate through. The refractive indices were determined *without evaporation* with the prism closed and with a small stream of the mixture flowing through the side of the prism. This prevented evaporation and gave a constant value. The refractive indices *with evaporation* were determined by dropping four drops of the mixture on the prism and allowing the mixture to remain exposed to the air for 20 seconds before closing the prism. Several points on both curves were determined. The points on either side of the constant evaporating mixture are as follows:—

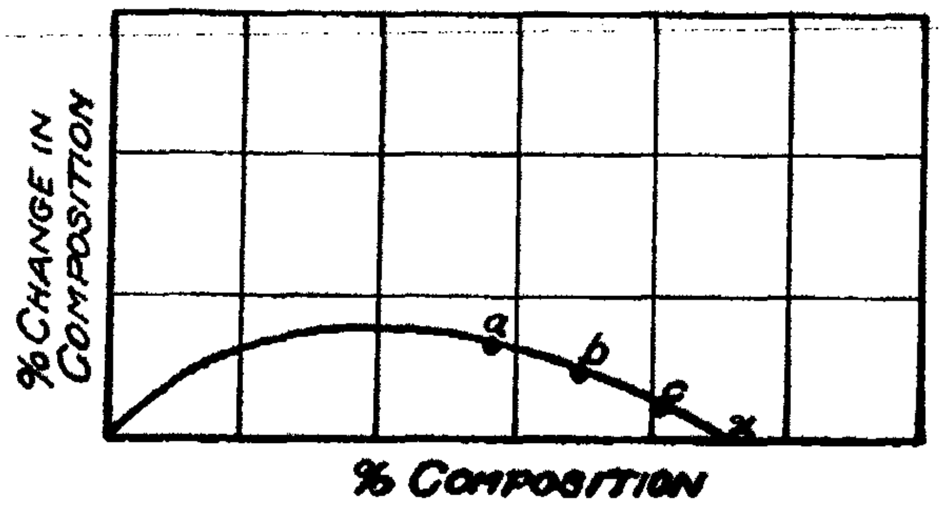

Fig. 3

% alcohol by volume	Refractive indices without evaporation	 with evaporation
30	1.4290	1.4308
10	1.4515	1.4504

The Third Method

Determination of the Constant Evaporating Mixture by an Air Bubbling Method

The principle of the third method is to pass a certain volume of air at a definite temperature and pressure through mixtures of the liquids and then determine the change in composition. If this change is plotted against the original composition as in Fig. 3, we are able to locate the point "x" which gives us the composition of the mixture which does not change on evaporation. Thus it would be possible by determining the points "a", "b", and "c", for instance to locate with some accuracy the constant evaporating mixture at "x".

The apparatus which we worked out for studying this method is without doubt much more elaborate than would be needed for an approximate determination. It was our purpose to attempt to control all variables at the start and then eliminate such parts of the apparatus as were unnecessary for an approximate determination. In Fig. 4:—

"A" is a large carboy with an automatic pressure regulator fastened at "a". "b" is the intake from the laboratory supply of air. This gives a constant pressure air supply.

"B" regulates the flow of air through the apparatus.

"C", "D", "F" and "G" are stabilizer bottles.

"E" is a flow meter.

The bottle "G" contains $CaCl_2$ for drying as do drying cylinders "H" and "K".

"J" is an automatic regulated thermostat.

"I" is the bubbler bottle which contains the liquids.

"L" controls the pressure in the apparatus.

"M" is a water manometer.

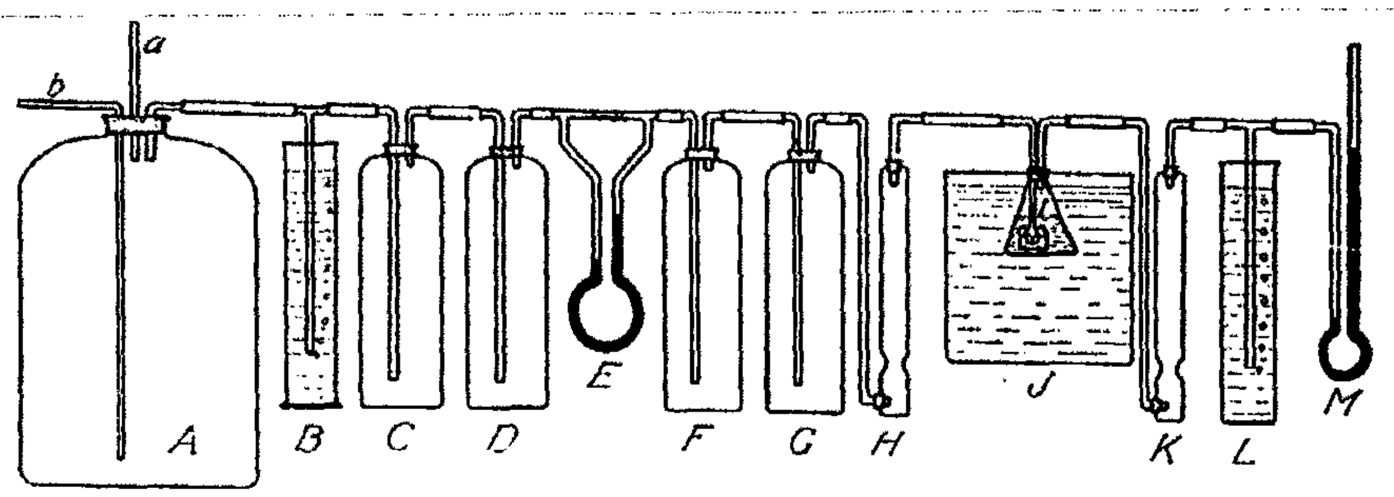

Fig. 4

50 cc of the carbon tetrachloride—alcohol mixtures were placed in the bubbler in the thermostat set to run at 20°. The pressure regulator "L" was set so that the sum of the barometric pressure and the pressure recorded on "M" was always equal to 760 mm of Hg. Air was then passed through at a definite rate recorded at "E" for a definite time taken with a stop watch. The change in composition was determined by taking the density of the mixture, using a chainomatic Westphal balance. The balance was used in the constant temperature room. The mixtures were first brought to temperature in a thermostat and the densities were immediately determined. The densities were checked from time to time by use of a pycnometer. Densities so determined for use in analysis are as follows:—

% alcohol by volume	D_4^{20} of mixture	% alcohol by volume	D_4^{20} of mixture.
0	1.594	60	1.113
10	1.513	70	1.032
20	1.433	80	0.949
30	1.353	90	0.871
40	1.273	100	0.789
50	1.192		

Results are as follows:—

Composition of mixture in % alcohol by volume		
before	after	difference.
100	100	0
90	93.4	3.4
80	84.9	4.9
70	75.7	5.7
60	65.6	5.6
40	43.9	3.9
30	32.5	2.5
20	20.6	0.6

Plotting these values as seen in Fig. 5, Curve III the constant evaporating mixture should be 17.4% alcohol by volume. Such a mixture was then made up and placed in the bubbler. After evaporating off about 17% of its weight the composition was still constant at 17.4%.

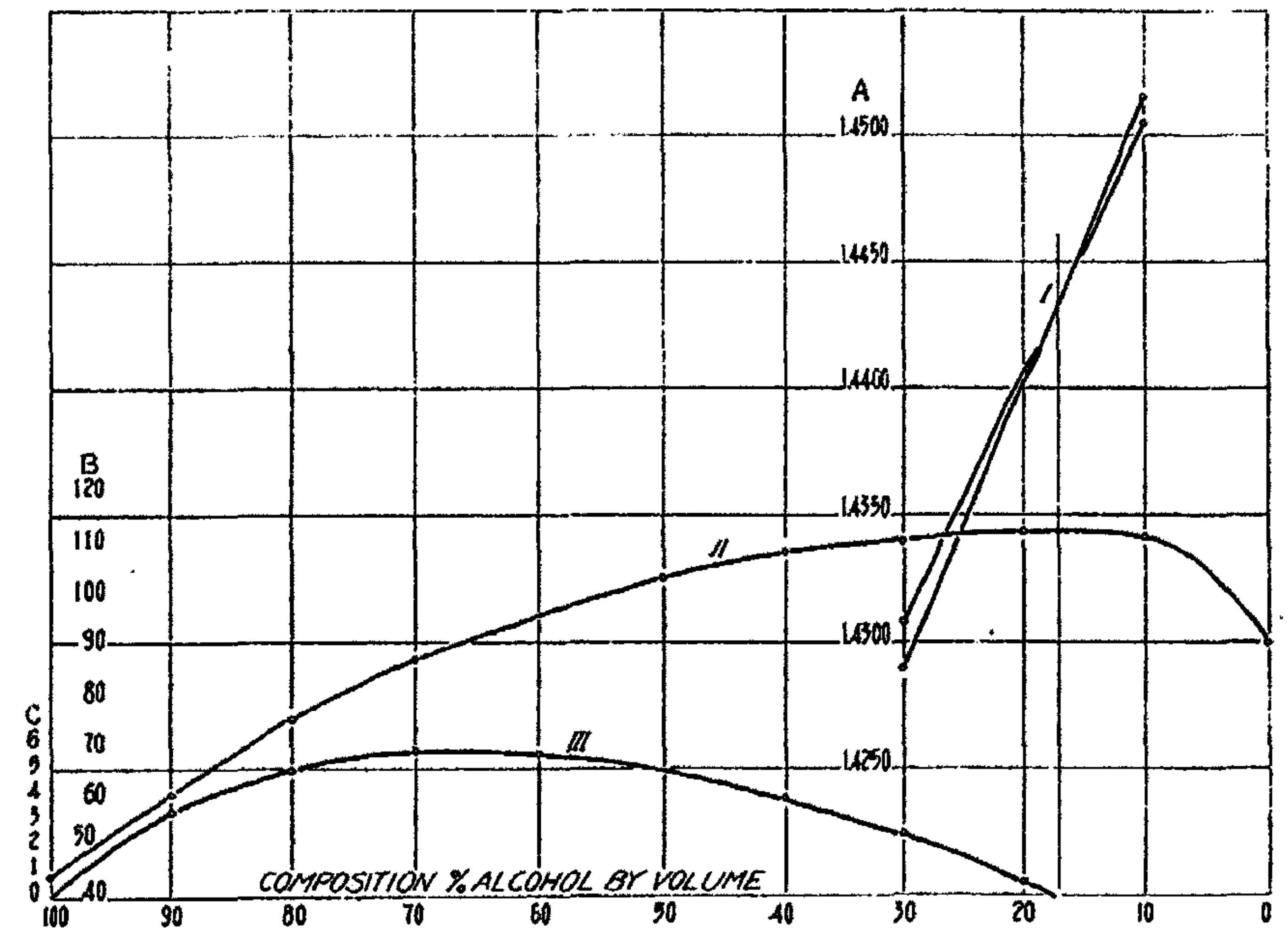

Fig. 5

Conclusion

In Fig. 5 are plotted the results of the determinations. On the abscissa is plotted the % composition by volume of alcohol for all three curves. For Curve I the ordinate is in refractive indices seen in column "A". For Curve II the ordinate is vapor pressure seen in column "B". For Curve III the ordinate is in % change in composition seen in column "C". It is quite apparent that the composition of the mixture corresponding:—

1. to the intersection of the refractive indice curves
2. to the intersection of the change of composition curve with the composition axis
3. with the one of maximum vapor pressure are all the same.

We hope to be able to simplify the air bubbling apparatus so that a much more rapid method will be available for the approximate determination of the constant evaporating mixture. It is to be noted that this method is not an air saturation method. Equilibrium conditions need not necessarily be reached as the values measured are relative.

The second method is limited in its application to those liquids which have a considerable difference in their refractive indices. If a physico-chemical method of analysis is used in the third method, the method is limited in its application to those liquids which have some property which is different enough for use in analysis.

Summary

1. We have modified the "submerged bulblet" method of Smith and Menzies for use in the rapid determination of vapor pressure of liquid mixtures.

2. The vapor pressure curve for $CCl_4-C_2H_5OH$ at 20° is given.

3. Densities at 20. degrees referred to water at 4 degrees of $CCl_4-C_2H_5OH$ mixtures are given.

4. A very simple method for approximately locating the constant evaporating mixture of two liquids by use of the Abbe refractometer is given. The mixture for carbon tetrachloride and alcohol has been determined.

5. An air bubbling method for determining the constant evaporating mixture of liquids is given and the mixture for carbon tetrachloride and alcohol has been determined by this method.

Williamstown, Mass.
July 1, 1923

THE MOLAR WEIGHT OF SELENIUM DIOXIDE IN ETHYL ALCOHOL

BY EDMUND BRYDGES RUDHALL PRIDEAUX AND GERALD GREEN

The Molar Weights of Oxides in Solution

There are few oxides of the non-metals, solid or liquid at ordinary temperatures, which dissolve as such in solvents other than water without chemical action.

The following may be quoted.[1]

Oxide	Formula Weight M	Solvent	Molar Weight observed M′
N_2O_4	92	acetic acid	90.3—94.6
N_2O_5	108	phosphoryl chloride	108.7—108.2
P_4O_6	220	naphthalene	218
P_4O_6	220	benzene	227
As_4O_6	394	sulphuric acid	288—455
As_4O_6	396	benzene	associated
Cl_2O_7	182.9	phosphoryl chloride	167—193
$Se\,O_3$	127	phosphoryl chloride	135—136[2]

From the foregoing figures, obtained by the cryoscopic method, it appears that association, which is usual in the vapour state in the case of acid anhydrides, exists also when the same compounds are in solution.

Selenium Dioxide in Alcohol

The case of selenium dioxide is particularly favourable, as being the oxide of a strongly electronegative element, which is readily soluble in alcohols (unlike tellurium dioxide) and does not, according to our experience, dehydrate them appreciably (unlike sulphur trioxide). v. infra.

Preparation of the Selenium Dioxide

A sample of the element in the form of powder, supplied by the courtesy of the Baltimore Copper Smelting Company, as arranged by Professor Victor Lenher of the University of Wisconsin, was oxidised by the different methods which are described in the literature.

(1) The method of Divers and Haga[3]. The selenium is oxidised by concentrated nitric acid, evaporated several times with more nitric acid and, after heating nearly to its subliming point, is resublimed in a current of dry oxygen. The product consists for the most part of very small, pinkish crystals.

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[1] See Turner's "Molecular Association."

[2] Worsley and Baker: J. Chem. Soc. 123, 2872 (1923).

[3] J. Chem. Soc. 75, 538 (1899).

(2) By direct combination with oxygen. This gives products which vary according to the temperature of sublimation and other conditions from pink to red, and also greyish needles of a gritty nature.

(3) By oxidation in presence of oxides of nitrogen according to the procedure of J. Meyer[1]. A current of oxygen was passed through a wash-bottle containing nitrite and acid. The selenium burnt at first to give a chocolate or dirty grey product. This gradually became lighter and finally gave a mass of colourless crystals like snow. When this material was heated again in pure oxygen it lost its crystalline form and brownish fumes were observed. On sublimation it gave a greenish vapour which condensed in slender needles. A part sublimed as the pink compound, but sufficient of the colourless was also obtained for use in the experiments. An analysis gave the following results.

An analysis gave the following results:

SeO_2	0.4046	0.4561	0.2362
Se	0.2886	0.3246	0.1693
% Se	71.33	71.17	71.25

Theory requires 71.22.

The Preparation of Dry Alcohol

Thorough dehydration of the alcohol was necessary, in order to ensure that no appreciable amount of selenious acid should be present, in the more dilute solutions. In the more concentrated the conversion of a small proportion into selenious acid would have little effect. The alcohol used in most of the experiments had been refluxed over lime for about 8 hours and allowed to stand in contact with aluminum amalgam according to the procedure of Wislicenus and Kauffman which, contrary to the opinion of Konowalow[2], we found to be effective. The alcohol boiled at 78.35° under normal pressure. After treatment with calcium carbide, refluxing and redistillation, it boiled at 78.38°. When dry selenium dioxide is dissolved in alcohol which has been purified thus, it reddens litmus paper. We attribute this to a trace of moisture, which forms selenious acid. We have found that the most effective drying agent is selenious oxide itself. The dry oxide is dissolved in the sample which is then distilled through freshly ignited lime. When the oxide is dissolved in this distillate it does not redden litmus. This alcohol, free from SeO_2, was used in some of the experiments.

Determination of the Molar Weight. Experimental

The type of Beckmann apparatus employed consisted of a double walled glass solvent vapour jacket and an inner boiling tube, into the bottom of which was sealed a stout platinum wire. Into the slanting side tube there passed a water cooled condenser. The selenium dioxide was introduced through a short vertical tube passing through the cork with the thermometer. The dry alcohol, prepared as already described, boiled at 78.39° under normal

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[1] Ber. 55, 2052 (1922).

[2] Pharm. Z. Russ. 35, 328.

pressure. About 25 c.c. was weighed into the corked tube and boiled for about an hour until the temperature remained sufficiently constant. The selenium dioxide, weighed in a glass tube was sent straight into the liquid by tapping. The side condenser was fitted with a drying tube.

First series. The weight of the alcohol was 21.338 grams and from this 0.20 grams has been deducted in making the calculations. The molecular weights have been calculated from a constant of 11.9 and the individual variations do not show any definite trend, except in the last three results, which refer to very concentrated solutions. The arithmetical mean of these molar weights is 122.

Second series. The weight of alcohol was 23.508 − 0.2 grams, the barometric pressure was normal and practically constant. The molar weights again show no trend. The most concentrated solution is that at which the molar weight begins to decrease in the first series. The arithmetical mean of these molar weights is 121.

First Series		*Second Series*	
Grams SeO_2 in 100 alcohol	Δt	Grams SeO_2 in 100 alcohol	Δt
0.43	0.043		
1.31	0.12		
1.77	0.162	1.62	0.165
2.925	0.29	2.85	0.295
3.71	0.36	4.39	0.425
4.85	0.46	6.02	0.585
5.77	0.54	7.59	0.735
6.80	0.612	9.60	0.985
9.30	0.877	12.15	1.195
11.1	1.048	14.53	1.385
13.7	1.395	17.1	1.63
17.85	1.77	19.7	1.915
19.05	1.88	22.0	2.105
23.1	2.23	24.48	2.335
27.3	2.64	27.27	2.601
31.0	2.995	32.67	3.04
35.0	3.363	37.9	3.475
38.0	3.675	44.25	3.995
41.6	3.929	48.6	4.515
45.8	4.249	54.4	5.097
49.5	4.731		
54.1	5.312		
56.6	5.876		
64.9	6.444		
69.5	7.054		

Results of Molar Weight Determinations

If the values of 'w' or 100/W = grams of SeO_2 to 100 grams of alcohol are plotted against Δt=elevation of the boiling point the best line for each series is obtained graphically, the following values of $W/\Delta t$ are deduced.

First Series	Second Series	Dilute Solutions to w = 25
10.46	10.7	10.28

The third value reproduces most accurately all the observations and we have taken $w/\Delta t$ as 10.3.

The constant molar elevation in alcohol (100 grams) is given in the most recent edition of Landolt and Börnstein's Tables as 12.0 (from substances of known molar weight) and 11.9 (from thermal data). Since the former value represents an average, and may include an excess of positive or negative deviations, we have chosen the latter.

Hence our observed molar weight is 122.6, as compared with a formula weight of 111.2.

Possible Formation of Ethyl Selenite

We have observed few signs of chemical action. There is a slight reduction after prolonged boiling, shown by the formation of a small reddish deposit. There is no formation of bubbles of ethylene, nor is the solution acid when both materials are perfectly dry. The question whether there is any formation of mono-ethyl selenite by the reaction:

$$SeO_2 + C_2H_5OH = SeO(OH)OC_2H_5 -$$

is somewhat more difficult to decide. This substance however would probably react acid to litmus.

Hinsberg[1] claims to have prepared a solid of this composition by evaporation of an alcoholic solution in presence of calcium chloride. But the alcohol is very loosely combined, it is lost when the substance is kept in a vacuous desiccator and is difficult to distinguish from alcohol of crystallisation. The molar weight in the more dilute solutions would not be affected by the formation of this compound, and if it were progressively formed in the more concentrated solutions, there would be a very decided fall; the molar weight corrected for solvent thus abstracted would be over 160. Although perhaps the lowness of the values in the case of the three most concentrated solutions may perhaps be attributed to a slight degree of combination with the solvent, yet the constancy of the remaining results seems to render it unlikely that this effect is important. If this solvation is ruled out, the results show a constant degree of polymerisation of the selenium dioxide over a wide range of concentration, quite similar to that observed in the case of boric acid[2] dissolved in water. The extrapolation of these results to high dilution led

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[1] Ann. 259, 40 (1890).

[2] Beckmann: Z. physik. Chem. 6, 460 (1890).

to molar weight of 67.2 instead of 62 for H_3BO_3. It was considered that they showed a normal molar weight, and the apparent association was attributed to the volatility of the solute.

No correction however was introduced. In the present case we have obtained some additional data with a view to supplying this correction. It is derived from a consideration of the vapour pressures of the pure solvent, the solution, and the partial pressures of solvent and solute. Using the symbols and equations as given in 'Problems in Physical Chemistry':

$$\Delta t \text{ (observed)} = \frac{RT^2 \ (r_L - r_v).}{Q}$$

This may be transformed into—

$$m = \Delta t_m / \Delta t \times \frac{100w}{W} \times (1 - r_v/r_L);$$ in which capital letters refer to the solvent, and r_v are the weight ratios of solute to solvent in the vapour, which must be found by analysis.[1]

The first series of distillations was carried out in the Walker-Landsberger boiling point apparatus. After some practice it was found possible to keep the volume of the liquid in the graduated tube constant by regulating the heating of the flask which supplied the alcohol vapour, and of the water bath which surrounded the outer jacket. A series in which the tube leading away the vapours projected a short distance outside the heated area before sloping downwards, showed very distinctly the effect of refluxing, the values of r_v/r_L being only 1/5 to 1/10 of those in the other experiments. In the second series the whole still-head was enclosed in a steam jacket, the solution being heated by the vapours of boiling alcohol as before. The solutions at the beginning and the end of the distillation, and the distillates were analysed, and their densities were determined.

The total weight of SeO_2 found in residue and distillate, 16.10 grams agreed well with the amount taken, 16.13 grams, and the agreement was also good in the other experiments.

Composition of solution at beginning is	90.5	SeO_2 in 100 alcohol
“ “ “ “ end	82.5	“ “ “ “
“ “ “ mean	86.5	“ “ “ “

The other experiments were checked in a similar manner.

An upper limit to the values of r_v may be obtained from the vapour pressures[2] of pure SeO_2. In the most concentrated solutions $w = 87$, $p = 15$ m.m, $P - p = 735$ $r_v = 0.0204$, $r_L = \ = 0.359$, $1 - r_v/r_L = 0.943$ and $m = 115.9$. But at lower concentrations the partial pressure of selenium dioxide in the vapour

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[1] In the determination of r_V/r_L the point at issue is assumed *i.e.* that the solute has a normal molar weight in the dissolved state. In cases of only slight association, this gives a first approximation, which is well within the limits of experimental error in the present case.

[2] Janneck and Meyer: Z. anorg. Chem. **83**, 51 (1913).

is far lower than that of the vapour in equilibrium with the solid; for at $w=31$, $m=104$ & at $w=12$, $m=79.5$, follow from the above calculation.

Solution SeO_2 in 100	Distillate SeO_2 in 100	r_V/r_L	$1-r_V/r_L$	m(corrected)
First Series				
61.9	2.93	0.0475	0.9525	116.7
31.05	1.77	0.057	0.943	115.9
11.9	0.509	0.0426	0.9574	117.2
Second Series				
86.5	2.90	0.0335	0.9665	118.8
45.7	2.72	0.0595	0.945	115.8
15.35	1.15	0.075	0.925	113.6
Third Series				
77.1	1.02	0.01325	0.987	121
29.0	0.73	0.0251	0.975	119.5
8.91	0.255	0.0286	0.971	119.2

These results on the whole show a diminution in molar weight with diminution in concentration. If equal weights are assigned to each, the mean of the expressions $1-r_V/r_L$ is 0.958, giving a corrected molar weight of 117.5. This corresponds to an association of 10% (double molecules). It will only be possible however to determine by this method the precise amount of the correction by the use of a more perfect distillation apparatus and larger quantities of solution than were available.

Summary and Conclusions

The molar weight of pure selenium dioxide dissolved in dry alcohol has been determined by the elevation of the boiling point. The means of two series agree well with one another, and the most probable molar weight from all results is 122.6, when the constant is taken at 11.9. There is no trend in the molar weights up to a concentration of 55 grams in 100. The relations between the amounts of the dioxide in solution and vapour has been determined; the mean correction based on these reduces the molar weight to 117.5.

University College, Nottingham
May, 1924

PERMEABILITY OF MEMBRANES[1]

BY WILDER D. BANCROFT AND CHARLES GURCHOT

We call a membrane semipermeable when it lets one constituent of a solution pass through—usually water— and does not permit diffusion of the other constituent or of one or more of the other constituents. It has usually been assumed tacitly that the membrane remained semipermeable unless it was ruptured mechanically. There is already a good deal of evidence to show that this simple view is not adequate.

Barlow[2] has shown that alcohol makes a copper ferrocyanide membrane permeable to sugar though he attempts no explanation of the phenomenon. In fact he apparently did not test for the sugar but merely noted the decrease of osmotic pressure when the cell containing a sugar solution was placed in aqueous alcohol. "Experiments were performed with varying strengths of solutions, going up from fifteen percent alcohol by steps of five percent to seventy percent. Strengths below and above these limits were also used, all with the same result. This gradual increase in the strength of the solution was thought to be advisable, because it seemed not unlikely that when the alcohol was in great excess the sign of the osmotic current might change. In other words, the alcohol might become the solvent and the water the solute. This, however, was not found even when the water was present in very small quantity indeed."

Since sugar is insoluble in alcohol, it is clear that the alcohol cannot make the copper ferrocyanide membrane permeable to sugar by increasing the solubility of the sugar in the membrane. There must therefore have been a fundamental change in the membrane.

Another unexplained phenomenon is one studied by Czapek[3], a number of years ago. He found that there was an exosmosis with an accompanying transfer of tannin from cells of *Echeveria* when these were placed in aqueous solutions of different alcohols. The critical concentrations at which exosmosis took place varied at 15°—19° from fifteen volume percent with methyl alcohol to 10-11 percent with ethyl alcohol, 4-5 percent with isopropyl and normal propyl alcohols, 1-2 percent with isobutyl and normal butyl alcohols, and 0.5 percent with amyl alcohol. These are, however, the concentrations at which the surface tension of water has been lowered to 68-69 percent of its normal value. It is therefore sometimes stated that permeability occurs when the surface tension of the water has been reduced to about two-thirds of its normal value. This is going beyond the facts as now known, because allyl alcohol and tertiary butyl alcohol become effective at different surface tensions.

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[1] Preliminary paper presented before Section B of the British Association for the Advancement of Science at the Toronto meeting.

[2] Phil. Mag. (6) 10, 1; 11, 595 (1906).

[3] Ber. deutsch. bot. Ges. 28, 159 (1910).

Czapek considers that the behavior of these last two alcohols may be due to some secondary toxic action. "A good example of such secondary toxic actions occurs with acetic acid which causes permeability before the critical concentration [with reference to surface tension] has been reached because of the toxic action due to its being an acid. For the theory of narcotics it is especially important to establish that a large number of these substances become toxic when a surface tension is reached characteristic for each organism. Among these substances are to be classed the saturated alcohols with normal carbon chain; and also acetone and ethyl acetate. Among the esters there are a number, notably methyl acetate and ethyl formate which are characterized by special toxic action.

"In the typical alcohol action we are certainly dealing chiefly with a diffusion phenomenon. The tannin can only begin to diffuse outward when its solubility in the plasma film and in the external medium is somewhat greater than in the cell solution[1]. If this becoming soluble coincides with changes in the surface tension of all three media (outer liquid, plasma film, and liquid inside the cell), one seems justified in assuming that at the critical concentration [at which exosmosis begins] the surface tensions of the plasma film and the outside solution have become equal.

"If the plasma film were a chemically and physically homogeneous substance, our method would give us a means of determining the surface tension of the plasma film. It is not possible, however, to simplify to such an extent the factors governing diffusion in the cell. From what we know, the plasma film is a complicated, heterogeneous, colloidal film, in which, as Overton has shown so convincingly, lipoid-soluble substances play an important part. The increased permeability of the plasma film to the substances in the cell solution with lowered surface tension of the outer liquid may well be due to changes in the plasma film colloids at the surfaces in question. Perhaps somebody will later formulate this problem more exactly."

If Czapek had known that tannin is only in colloidal solution, he would probably have been able to take the next step himself. It does not seem to have occurred to him, however, to make any experiments to determine whether there had or had not been any permanent change in the membrane.

Walden[2] showed that tenth-normal solutions of formic, acetic, propionic, butyric, isobutyric, valerianic, cyanacetic, halogen-substituted acetic, glycollic, glyoxalic, methyglycollic, ethylglycollic, glyceric, alpha-oxybutyric, beta-oxybutyric, meta-oxybenzoic, para-oxybenzoic, diglycollic, quinic, tartaric, citric, mandelic, alpha-nitrophthalic, mellitic, tetra-carbonic, dimethylmalonic, quinolinic, acrylic, and caproic acids passed through the copper ferrocyanide membrane while the sodium salts of most of these acids did not. This is a very strange thing, because there is no apparent reason why organic acids should be soluble in copper ferrocyanide. As Walden was working empirically with no theory to guide him, it did not occur to him to test whether

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[1] [There seems to be no justification for this statement.]

[2] Z. physik. Chem. 10, 705 (1892).

the organic acids had, by any chance, caused any permanent change in the membrane.

Czapek[1] found that his plant cells (*Echeveria*) gave the exosmose reaction with concentrations of hydrochloric, sulphuric, nitric, phosphoric, oxalic, acetic, malic, tartaric, citric, lactic, fumaric, and salicylic acids at concentrations exceeding N/6400. It seems very improbable that a reaction involving hydrogen ion should occur at equimolecular concentrations of these acids and there is either a large experimental error or else some factor has been overlooked.

When we consider the permeability of the living cell, we find that no simple theory of permeability is adequate and that it is apparently necessary to postulate that a given cell[2] membrane is both permeable and impermeable for the same substance. A lipoid film will account for a great many of the phenomena; but it would not let water through, so we have to postulate an action due to lecithin. A great many of the acid dyes are insoluble in lipoids but penetrate certain cells readily. Worse than that, one finds that among the substances for which the cells are normally impermeable are grape sugar, fruit sugar, cane sugar and other carbohydrates, the amino-acids and the acid amides, and many other substances which are foodstuffs for the cells and which are brought into the cells from the outside. Höber says, rather despairingly, that "what the cell can use, it shuts out, and what it cannot use, it lets in."

This difficulty disappears completely if we assume that the permeability of the cell membrane depends on the surrounding medium and that relatively slight changes in the latter may make the cell membrane permeable or impermeable to a given substance. There is nothing especially new about this hypothesis. Years ago, Höber[3] suggested that the cell might be impermeable while at rest and permeable when active. The same point of view is apparently held by R. S. Lillie[4] and by Bayliss[5]. "It is a matter of great difficulty to suggest any probable structure for the membrane. Owing to its mode of production, it is no doubt of a very complex chemical nature. It appears to be in all states of the cell permeable to all substances soluble both in water and in oil or organic liquid, such as urea, some ammonium salts, alcohol, chloroform, carbon dioxide, oxygen, etc., as Meyer and Overton pointed out. In the resting state of the cell, the membrane is impermeable to salts, other than certain salts of ammonium, to glucose and to amino-acids, while in a state of activity it becomes permeable to all these."

The difficulty with this is that it is vague[6] and that there is no independent proof of the hypothesis as yet. If we consider a copper ferrocyanide membrane as a colloidal film—which is what it is—it is evident that anything

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[1] Ber. deutsch. bot. Ges. 28, 161 (1910).

[2] Höber: "Physikalische Chemie der Zelle und Gewebe," 476–544 (1922).

[3] "Physikalische Chemie der Zelle und Gewebe," 263 (1911).

[4] "Protoplasmic Action and Nervous Action," 347, 356 (1923).

[5] "Interfacial Forces and Phenomena in Physiology," 134 (1922).

[6] Lillie: "Protoplasmic Action and Nervous Action," 337 (1923).

which will coagulate the film will make it permeable. It seemed probable therefore that Barlow's experiments with sugar and alcohol could be explained on the assumption that alcohol coagulated the membrane. This was a point which could easily be tested experimentally.

Copper ferrocyanide membranes were made by a modification of Collander's method. Glass tubes were used, 3 cm in diameter and 10 cm long. One end was ground on each tube and covered with a layer of cheesecloth to serve as a support for the membrane. This end was dipped into a warm, ten percent, solution of gelatine freed from air bubbles by filtering through sand. The gelatine was allowed to dry on the cheesecloth, the tube being held downward after removing the excess of gelatine. It is immaterial if a few air bubbles persist in the gelatine film at this stage. When the gelatine film was dry, 2cc of the same gelatine solution, freed from air bubbles, were introduced inside the tube on top of the first gelatine layer. It is important that there are no bubbles in this layer. This upper layer was allowed to set to a stiff jelly but not to become bone dry and was hardened for twenty-four hours in a two percent solution of formeldehyde. The gelatine film was washed free of formaldehyde in several changes of distilled water, the tubes being allowed to stand for about two hours in each change of water. The tubes were then suspended in tumblers or beakers by means of large corks bored to fit the glass tubes. A fresh solution containing 0.02 mols potassium ferrocyanide was placed outside the membrane and a solution containing 0.02 mols copper sulphate was put inside the tube. In about half an hour, copper ferrocyanide began to form on the inner surface as a uniform, brown membrane. The reaction was allowed to run for twenty-four hours. Each membrane was tested by putting a one percent solution of cane sugar inside the tube and distilled water outside. The membrane was considered satisfactory if there was no test for sugar in the outside water after sixteen hours.

When a sugar solution was put on one side of the membrane and a dilute methyl alcohol solution on the other side, sugar passed through the membrane, thus confirming Barlow's results. Since the question of permeability may be to some extent dependent on the time factor, tests for the presence or absence of sugar were always made at the end of about sixteen hours. To show that a permanent change in the membrane had taken place, the membrane was exposed to aqueous methyl alcohol solutions and the membrane was washed with water. It was then found to be permeable to sugar in the absence of alcohol, showing that coagulation had taken place.

Less than two percent of methyl alcohol are sufficient to make the copper ferrocyanide membrane permeable to sugar. With the higher alcohols the necessary concentrations were much lower; but we are not prepared as yet to say to what extent the critical concentrations correspond to equal surface tensions. The results are in qualitative agreement, however, with those of Czapek and we feel certain that the permeability which he obtained with *Echeveria* was due to coagulation of the cell membrane.

A corollary from this is that methyl alcohol must coagulate a copper ferrocyanide sol and this proved to be true. The precipitation of the sol is a much less sensitive test than the one for the permeability of the membrane and it takes approximately forty percent methyl alcohol to coagulate a copper ferrocyanide sol under the conditions which we employed. Experimental details will be given in a later paper by Mr. Gurchot.

Similar experiments were also made with copper ferrocyanide membranes and solutions of acetic acid so as to confirm Walden's results. When solutions of acetic acid stronger than 0.5 percent have been in contact with a copper ferrocyanide membrane, the membrane is no longer impermeable to sugar and has therefore coagulated. In line with this is the fact that acids precipitate a copper ferrocyanide sol and alkalies peptize it. It is possible that the permeability of cell membranes after death is due to the increased acidity of the system.

A few experiments were made to regenerate the membrane by changing from an acid solution to an alkaline one; but no satisfactory results have been obtained. This is not essential because the materials which form the membrane in a plant cell or an animal cell are probably being supplied continually. A more interesting line of attack will be to repeat the preceding experiments with a little copper salt on one side of the membrane and a little ferrocyanide on the other side. Experiments of this sort will be started at once.

The general results of this preliminary paper are as follows:

1. Copper ferrocyanide membranes are coagulated by low concentrations of methyl alcohol and of acetic acid, thereby becoming permeable to sugar.

2. Barlow's experiments with alcohol, Walden's experiments with acids, and Czapek's experiments with alcohols and acids involved nothing more mysterious than a coagulation of the membrane.

3. Alcohols and acids coagulate a copper ferrocyanide sol while alkalies peptize a copper ferrocyanide gel.

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THE RELATION BETWEEN THE DEPOLARIZATION OF THE SCATTERED LIGHT AND THE KERR EFFECT IN LIQUIDS

BY W. H. MARTIN

The Depolarization Factor and the "Shape" of the Molecule

The theory of the scattering of light[1] by particles of dimensions small compared to the wave-length of light indicates that the light scattered at right angles to the direction of the exciting beam will be completely polarized only if the scattering particles be of spherical optical symmetry (optically isotropic).

Experiment has shown that the light scattered by dust-free gases[2] and liquids[3] is not completely polarized. Rayleigh[4], J. J. Thomson[5], King[6], Gans[7] and others have related the state of polarization[8] of the scattered light to certain parameters of the molecule expressing the "shape" of the molecule. For simplicity the molecules have been chosen as ellipsoids so that three parameters will suffice.

The Electrical Double-Refraction and the "Shape" of the Molecule

When a gas[9] or liquid[10] is placed in an electric or magnetic[11] field the material becomes doubly refracting. The theory which has successfully explained this property rests also on the hypothesis that the molecules are optically anisotropic and that these molecules tend to become oriented in certain directions by the imposed electric or magnetic fields. Langevin[12] and Gans[13] have developed this theory in a way to bring it into good agreement with all the known facts of electric and magnetic double-refraction. Their theory involves the same parameters of the molecule as are used in the theory of scattering, and makes it evident at once that fluids which have a high Kerr Constant should also have a large Depolarization Factor.

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[1] Lord Rayleigh: Phil. Mag., **47**, 375 (1899).

[2] Cabannes: Ann. Phys., **15**, 5 (1921); Lord Rayleigh: Proc. Roy. Soc., **94A**, 453 (1918).

[3] Martin and Lehrman: J. Phys. Chem., **26**, 75 (1922); Raman: Proc. Roy. Soc., **101A**, 64 (1922).

[4] Phil. Mag., **35**, 373 (1918).

[5] Phil. Mag., **40**, 393 (1920).

[6] Proc. Roy. Soc., **104A**, 333 (1923).

[7] Ann. Physik, **65**, 97 (1921).

[8] Throughout this paper we shall define the Depolarization Factor of the scattered light as the ratio between the intensities resulting from the component vibration in the plane containing the exciting and the scattered rays and the component vibration at right angles to this plane; the scattered light being observed in a direction at right angles to the direction of the exciting beam supposed parallel and unpolarized.

[9] Leiser: Verh. deutsch. physik Ges., **13**, 903 (1911); Lyon: Ann. Physik, **46**, 753 (1915).

[10] Kerr: Phil. Mag., **37**, 380 (1894), etc.

[11] Cotton and Mouton: Ann. Chim. Phys., **20**, 194 (1910), etc.

[12] Le Radium, **7**, 249 (1910).

[13] Ann. Physik, **64**, 481 (1921).

The Relation between the Kerr Effect and the Depolarization Factor

Richard Gans has correlated the theories of light-scattering and of electrical double-refraction for gases[1] and more recently for liquids[2], so as to eliminate the parameters of the molecule and give equations which involve only quantities which are capable of direct measurement. Gans' final result for liquids is:

$$\rho = \frac{48\pi\nu\lambda B}{\frac{1}{3}\beta(\nu^2-1)^2(\nu^2+2)^2\zeta + 56\pi\nu\lambda B} \qquad (1)$$

where:

ρ is the Depolarization Factor as defined above.

ν is the refractive index of the liquid for light of wave-length λ.

B is the Kerr Constant $= \frac{\nu_2 - \nu_1}{\lambda E^2}$, where ν_2 and ν_1 are the refractive indices for vibrations parallel and perpendicular respectively to the imposed electric field of strength E.

β is the isothermal compressibility of the liquid.

$\zeta = \frac{(\epsilon-1)\ (\epsilon+2)}{(\nu^2-1)\ (\nu^2+2)}$, where ϵ is the dielectric constant.

Gans has submitted his formula to experimental test for two liquids and has shown that for these cases the above equation holds very well indeed. It is the purpose of the present paper to test the relation further for a number of liquids for which ρ has been measured in this laboratory.

Measurements of the Depolarization Factor of the Scattered Light

The values of ρ are for the most part taken from a former paper[3]. Nitrobenzene and chloroform have been recently measured by observing the scattered light through a double-image Wollaston prism and equalizing the intensities of the images by rotating a Nicol prism (see J. Phys. Chem., **27**, pages 559-560 (1923)). The liquids as before were contained in Pyrex crosses and were rendered dust-free by the method of distillation in vacuum.

Nitrobenzene was chosen because its Kerr Constant is large and has been measured carefully by a number of observers. It was first purified by two recrystallizations. It could be readily distilled with the hot bulb of the distilling apparatus (see Fig. 1, J. Phys. Chem., **26**, 75 (1922)), at 75° although the liquid boils at 210°.

The depolarization factor for chloroform had been measured by Raman[4] but the measurement was repeated since the calculated and observed values of ρ for this liquid are in such very poor agreement. The liquid was freed of alcohol by shaking out with water and drying by distillation over potassium carbonate. It distilled at a very constant temperature (61.3°). It gave negative tests for hydrogen chloride, chlorine and phosgene and with sulphuric

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[1] Ann. Physik, **65**, 97 (1921).

[2] Z. Physik, **17**, 353 (1923).

[3] J. Phys. Chem., **26**, 75 (1922).

[4] Nature, **110**, 11 (1922).

acid and a little formaldehyde gave only the faintest trace of yellow. This purified chloroform gave a value of $\rho = 0.150$, in good agreement with Raman's value 0.155, so that it seems certain that the poor agreement between the observed and calculated values cannot be attributed to impurities in the chloroform nor to any error in making the measurement.

TABLE I

Liquid	All at 20° C.		ζ	ρ calculated	ρ(White light) Observed.
	$B \times 10^7$ $\lambda = 589\ \mu\mu$(*)	$\beta \times 10^6$ (per atmosphere)†			
Benzene	0.595(McComb)[1]	91	1.03	0.44	0.485
Toluene	0.78 (Lippmann)[2]	91	1.15	.50	.50
Xylene (commercial)	0.80 (Lippmann)	80	1.16	.50	.52
Chlorobenzene	9.8 (McComb)	75	22.3	.39	.48
Nitrobenzene	256. (McComb)	47.5	208.	.66	.68
Pentane	0.076(Bergholm)[3]	242	1.04	.090	.072
Hexane	0.085(Bergholm)	159	1.00	.13	.10
Chloroform	−3.41 (McComb)	100	6.71	.46	.15
Carbon tetra-chloride	0.073(Lippmann)	104.5	1.13	.09	.11 Raman‡
Methyl alc.	1.11 (Schmidt)[4]	122	350.	.011	.071
n-Propyl alc.	−3.64 (Bergholm)	100	143.	.066	.085
Isobutyl alc.	−4.10 (Schmidt)	100	111.	.087	.085
Ether	−0.80 (Schmidt)	183	6.66	.18	.10
Carbon bisulphide	3.17 (McComb)	93.2	0.975	.65	.70
Water	3.7 (Schmidt)	49.	2262.	.013	.086 (Martin) .12 (Raman) .12 (Gans)§

*B varies considerably with λ, but the function $\pi\nu\lambda B$ in equation (1) varies only slightly with λ, so that the calculated value of ρ varies only slightly with λ. See later paragraph on the dispersion of ρ.

†The unit must be changed from "atmosphere" to "dyne per cm^2" for use in equation (1).

[1] Phys. Rev., 29, 535 (1909).

[2] Z. Elektrochemie, 17, 15 (1911).

[3] Ann. Physik, 54, 511 (1918).

[4] Ann. Physik, 7, 142 (1902).

‡Raman and Rao: Phil. Mag., 45, 625 (1923).

§Professor Raman has intimated in conversation that the higher values of ρ obtained by Gans and himself are due to a slight fluorescence which he finds present even in the most carefully distilled water and which is excited by the longer ultraviolet rays. This fluorescence was not a disturbing factor in the author's result since the source of light was a carbon arc or a Pointolite lamp, either of which gives a light which is much yellower than the sunlight used by both Raman and Gans.

When the light which excited this fluorescence is screened out Raman finds a value of ρ for water of approximately 0.09.

The sources of the Kerr Constants used in the calculations are indicated in the table. McComb's absolute values are used where possible. Bergholm's relative values are converted to absolute values by equating his and McComb's values for benzene. The values of the Kerr Constants cannot be taken as very exact since the values found by various investigators differ in some cases by as much as 50 percent. Certainly ρ is known with greater accuracy than B.

The other physical constants used in the calculations are taken from Landolt-Börnstein tables (1923 edition).

Considering the uncertainty in the value of the Kerr constants for many of the liquids, the agreement between the values of the depolarization factors calculated from equation (1) and the observed values may be considered as satisfactory for all liquids except chloroform, methyl alcohol, and water. The Kerr constants for methyl alcohol and water have been measured apparently only by Schmidt, but for chloroform measurements have been made by McComb, Lippmann and Schmidt and their results are in fairly good agreement, so that the formula seems here to present a real difficulty.

Gans places a limitation on his formula " . . . Our conclusions hold only for fluids whose molecules have no permanent electric moment in the Debye sense." This does not, however, appear to be a satisfactory way out of the difficulty unless water, methyl alcohol and chloroform have other properties which would differentiate them from the majority of liquids. The formula holds so remarkably well, that special interest attaches to these cases for which it conspicuously does not hold.

The Dispersions of the Kerr Constant and the Depolarization Factor

It has been established that for all liquids which have been examined[1] the dispersion of the Kerr constant is well given by the Havelock formula[2].

$$\frac{B\lambda\nu}{(\nu^2-1)^2} = \text{a constant.}$$

Writing equation (1) in the form

$$\rho = \frac{\dfrac{48\pi\nu\lambda B}{(\nu^2-1)^2}}{\frac{1}{3}\beta(\nu^2+2)^2\zeta + \dfrac{56\pi\nu\lambda B}{(\nu^2-1)^2}}.$$

it follows that the dispersion of ρ is given by the relation

$$\rho_\lambda = \frac{k}{\frac{1}{3}\beta(\epsilon-1)\ (\epsilon+2)\dfrac{\nu^2+2}{\nu^2-1} + \dfrac{7}{6}k} \qquad (2)$$

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[1] McComb: Phys. Rev., 29, 525 (1909); Cotton and Mouton: Ann. Chim. Phys., 19, 153 (1910); 20, 194 (1910).

[2] Proc. Roy. Soc., 80A, 28 (1907).

To test formula (2) a few preliminary measurements on the value of the depolarization factors of nitrobenzene for the blue, green and yellow mercury lines have been made. The source of light used was a quartz-mercury "Labarc" lamp and the lines were isolated by Wratten mercury monochromatic light-filters. The scattered light was photographed through a Wollaston and a Nicol prism, after making a preliminary setting of the Nicol visually. Three pictures, one for each of the three lines, were made on the same Wratten Panchromatic plate.

A great difficulty is the length of exposure necessary when monochromatic light is used. Using a Pointolite lamp as the source an image of suitable density may be obtained in ten minutes exposure, but with the mercury lamp and Wratten filters several hours exposure are necessary. Only six successful exposures have been made, two for each of the mercury lines. The results of the photometry of the images appear in Table 2 along with the values of ρ calculated from equation (2).

TABLE II

λ	ρ for nitrobenzene Calculated from (2).	ρ Observed.
4359Å	0.662	0.684
5461	0.655	0.679
5780	0.654	0.684

The only conclusion to be drawn is that, within the experimental error, the values of ρ for the three mercury lines are the same. The results are at least not in disagreement with the theory since the change in ρ predicted by equation (2) is too slight to be observed in these experiments. The use of ultraviolet light suggests itself as a means of obtaining an observable dispersion but almost all these liquids which scatter light to any appreciable extent fluoresce in the ultraviolet. To differentiate between fluorescence and scattering would require spectroscopic methods, and this would again greatly increase the length of exposure required.

Does a Magnetic Field affect the Depolarization Factor?

If the hypothesis of anisotropic molecules be advanced to explain the two phenomena of electric double-refraction and of imperfect polarization of the scattered light, then it follows that an imposed electric or magnetic field, since it tends to orient the molecules, should cause a change in the depolarization factor of the scattered light.

To estimate approximately the magnitude of the effect to be expected we may follow the reasoning of Cotton and Mouton[1]. With the strongest obtainable magnetic fields they found that the difference of refractive indices

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[1] Ann. Chim. Phys., 19, 183 (1910).

for the two components of the doubly-refracted ray was only 1/10000 of the difference between the two rays as given by a crystal. If we assume the molecules in the crystal to be oriented in some perfectly regular fashion, then we may say that the orienting effect of the magnetic field on the liquid is only such as to disturb very slightly the normal random orientation of the molecules in the liquid. It seems then that theory would anticipate no measurable change in ρ in any obtainable magnetic or electric field.

The argument summarized above seemed however not sufficiently convincing to discourage experimental test and some measurements have been made of the depolarization factor of nitrobenzene in a magnetic field. A magnetic field was preferred because of the danger of decomposition of the liquid in an electric field. Nitrobenzene was again chosen because of its relatively large magnetic double-refraction and also because it scatters so much light as to make the measurement of ρ comparatively easy.

A large electromagnet was borrowed from the Physics Department. The poles of this magnet, shown in section in the figure, already had holes bored through their centers to enclose a small mercury lamp for demonstrating the Zeeman effect. New nose-pieces were made for the poles which exactly fitted the arms (diameter 1.5 cm.) of the glass cross containing the dust-free nitrobenzene. The field coils of the magnet would carry about 12 amps. and at this current the magnetic field at O with the cross removed was 5000 Gauss.

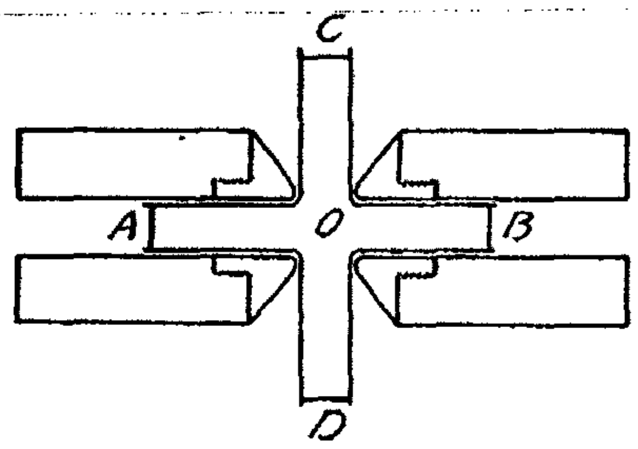

FIG. 1

The exciting light from a Pointolite lamp could enter through either AB or CD and the scattered light could be observed through the other arms. The values of the depolarization factor were measured visually as described above.

Alternate readings taken with the magnetic field on and off failed to discover any effect whatever of the magnetic field on the value of the depolarization factor. This was true whether the exciting light was parallel to or perpendicular to the magnetic field. It seems safe to say that within 2 percent value of ρ for nitrobenzene is not affected by a field of 5000 Gauss.

The author wishes to express his thanks to Professor J. C. McLennan for the use of the electromagnet, and to Mr. H. J. C. Ireton, who made the measurements of the field strength.

Summary

Richard Gans' theory of the relation between the Depolarization Factor of the scattered light and the Kerr Constant of electric double-refraction is submitted to experimental test for fifteen liquids.

The values of the Depolarization Factors calculated from theory agree well with those measured in this laboratory in almost all cases. For chloroform, water and methyl alcohol however the disagreement between theory and experiment is very striking.

Theory suggests that the Depolarization Factor must be affected by a magnetic or electric field, though the magnitude of the change anticipated by the theory appears to be quite small. Measurements of the Depolarization Factor for nitrobenzene made in a magnetic field of 5000 Gauss failed to discover any change in the degree of polarization of the scattered light.

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University of Toronto,
June, 1924.

THE INTERFACIAL TENSION OF SOME AQUEOUS SOLUTIONS AGAINST OILS, AS CORRECTED FOR SPECIFIC GRAVITY

BY R. L. HOWARD AND TORALD SOLLMANN

I. Introduction

During the investigation of certain phenomena of emulsification, it became necessary to determine the influence of a series of substances of biologic interest on the surface or interfacial tension between water and oils. This was done in the customary manner by counting the number of drops that are delivered when a given volume of oil is allowed to flow upward through an aqueous solution; employing the special pipette described by Donnan.[1] Anything which lowers the interfacial tension between oil and water hastens the formation and detachment of drops at the tip of the pipette; so that the drops are the smaller, and the drop-number is the greater, the lower the interfacial tension. Conversely, increase of the interfacial tension is indicated by decrease of the drop-number.

The interfacial tension between an aqueous solution and an oil would therefor vary with the factor $= \frac{\text{drop number in water}}{\text{drop number in oil}}$. In this the interfacial tension of water against the same oil is taken as unity.

This simple formula, however, requires a correction for specific gravity; for it is self-evident that an oil drop will detach itself the more readily, and therefor be the smaller, the greater is the difference in specific gravity between the oil and the solution. The influence of this factor is relatively insignificant for substances which produce large changes in interfacial tension; such as soaps or alcohol; but with salts, sugar etc., the influence of specific gravity is vastly greater than the effect on true interfacial tension. In their case, the simple formula would lead to quite erroneous conclusions. The need of this correction is perhaps not generally appreciated although it has been used by Harkins[2] and also by Lewis[3]. Specific gravity is always taken into account in the determination of "surface-tension," i.e., the interfacial tension between a liquid and air. There the formula reads[4]:

Surface tension of solution $= \frac{\text{Specific Gravity of Solution} \times \text{Drop Number of Water}}{\text{Drop Number of Solution.}}$ (taking the surface tension of water against air as unity). The corresponding formula for the interfacial tension of a solution against an oil should read:

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[1] Z. physik Chem. 31, 42 (1899).

[2] Harkins and Humphrey: J. Am. Chem. Soc., 38, 236 (1916).

[3] Lewis: Phil. Mag. (6), 15, 499.

[4] McClendon: "Physical Chemistry of Vital Phenomena", 59.

$$\text{IFT} = \frac{\text{drops W}}{\text{drops S}} \times \frac{\text{grav. S} - \text{grav. Oil}}{\text{grav. W} - \text{grav. Oil}}$$

In this, *IFT* stands for the *corrected interfacial tension*, relative to water = 1; *drops W* = number of drops formed in water; *drops S* = number of drops formed in the solution, *grav. S* = specific gravity of the solution; *grav. Oil* = specific gravity of the oil; and *grav. W* = the specific gravity of water, *i.e.* 1.000.

The following data illustrate the application of this formula. In interpreting these it must be borne in mind that our Donnan pipette delivers against distilled water 45.2 drops of liquid petrolatum, and 73 drops of olive oil (alcohol-extracted). An observational error of one drop will therefore change the interfacial tension by 2.2 percent for liquid petrolatum; and by 1.4 percent for olive oil. Changes smaller than these must be looked upon with suspicion, as within the possibility of observational error.

II. *The influence of specific gravity on the apparent interfacial tension of sodium chloride and of sugar solutions:*

This is illustrated by the experiments of Table I, from which it will be seen that the uncorrected, or more properly "false" interfacial tension of the 0.5M sodium chloride is some 13 percent less than that of the 0.07M solution, which would be quite a material difference. The true interfacial tension, however differs by only 0.4 percent, which is well within the observational error. This range of concentration of sodium chloride therefor has practically no effect on the interfacial tension.

For the sugar solutions, between 0.03 and 0.16 mol, the "false" interfacial tension also decreased by 14%; the true interfacial tension by 3%—a very little beyond the experimental error.

TABLE I

Apparent and Corrected Interfacial Tension of Sodium Chloride and Sucrose Solutions against Liquid Petrolatum[1]

Solution	Mol. Conc.	Uncorrected *IFT* $\frac{\text{Drops Water}}{\text{Drops Solution}}$	Sp. G. of Solution	Corrected *IFT*[2]
NaCl	0.070	0.978	1.0032	1.006
NaCl	0.317	0.902	1.0127	1.004
NaCl	0.506	0.854	1.0196	1.002
Sucrose	0.028	0.963	1.0033	0.991
Sucrose	0.103	0.881	1.0116	0.971
Sucrose	0.163	0.821	1.0193	0.961

III. The Corrected Interfacial Tension of the Salts of the Hofmeister Series:

These were compared in M/8 solutions, (to approximate somewhat the osmotic pressure of frog's blood). The results are shown in Table II. The surface tension of the solutions (water = 1) is included in the last column for comparison.

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[1] Specific Gravity 0.8873.

[2] This term will be used throughout to designate the formula explained above, *i.e.* applying the correction for specific gravity.

It will be seen that none of the salts alter the interfacial tension toward liquid petrolatum by more than 2.5%; i.e. they are essentially within the experimental error. With the olive oil, the changes are somewhat greater, namely +4 to −6 percent for inorganic salts and acids; −9 percent for sucrose; and −28 percent for sodium citrate. The citrate effect is presumably due to the formation of soap by OH ions.

TABLE II

The Influence of Equimolecular (M/8) Solutions of the Salts of the Hofmeister Series on Interfacial Tension; (toward Liquid Petrolatum and toward Olive Oil); and on Surface Tension (toward Air)

Solute	IFT (corrected) Liquid Petrolatum (1)	IFT (corrected) Olive Oil (2)	Surface Tension (air)
Water	1.000	1.000	1.000
Sucrose	0.986	0.911	
NaI	1.000	0.966	1.015
NaBr	0.996	0.944	1.014
NaCl	0.981	0.970	1.013
Na_2SO_4	1.001	1.027	1.015
NaCitrate	0.975	0.722	1.007
Na_2CO_3	0.998		1.019
HCl M/80 in NaCl, M/16	1.000	1.039	1.013
$CaCl_2$ M/80 in NaCl M/16	0.991	1.002	1.017
$BaCl_2$ M/80 in NaCl M/16	0.988	0.981	1.012

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[1] Liquid Petrolatum of Specific Gravity 0.8873.

[2] Olive oil, extracted by alcohol, Specific Gravity 0.916.

The effect of these solutes on surface tension is also small, namely +0.7 to 1.7 percent.

It must therefor be concluded that the changes of interfacial tension between M/8 solutions of the Hofmeister series and liquid petrolatum are so slight that they fall within the limits of error of the Donnan pipette. The interfacial tension toward olive oil is definitely, but still only slightly lowered by most of the salts; but sodium citrate produces a quite considerable lowering, presumably by forming soap.

The insignificance of these salts for interfacial tension is also illustrated by the practical identity of the corrected and uncorrected interfacial tension $\frac{\text{(drops W)}}{\text{(drops S)}}$ when solutions of approximately equal specific gravity are compared. This is is shown in Table III.

TABLE III

Interfacial Tension of Hofmeister Series, with Solutions of approximately equal Specific Gravity, toward Liquid Petrolatum[1]

Solution	Mol. Conc.	Specific Gravity	$\frac{\text{Drops W}}{\text{Drops S}}$	IFT corrected
NaI	0.131	1.0118	0.967	1.012
NaCl	0.317	1.0127	0.917	1.020
Na_2SO_4	0.949	0.0119	0.906	1.001
NaCitrate	0.617	1.0116	0.923	1.017
Na_2CO_3	0.106	1.0113	0.923	1.016

[1] Liquid Petrolatum Specific Gravity = 0.887.

It may be added that Harkins[1] finds the interfacial tension between water and benzene but very slightly increased by sodium chloride 0.5 moles per liter.

IV. The Interfacial Tension of Non-electrolytes:

Table IV shows that urea and sucrose lower the true interfacial tension toward liquid petrolatum but slightly—perhaps just beyond the experimental error. Glycerol, chloral and especially alcohol lower the interfacial tension very materially.

TABLE IV

The Interfacial Tension of Non-electrolytes toward Liquid Petrolatum[1]

Solution	Mol. Conc.	Specific Gravity	$\frac{\text{Drops W}}{\text{Drops S}}$	IFT corrected
Urea	1.538	1.0121	0.883	0.978
Sucrose	0.163	1.0193	0.854	0.961
Glycerol	0.575	1.0112	0.816	0.899
Chloral Hydrate	1.515	1.0109	0.709	0.776
Ethyl Alcohol	4.56	0.9693	0.528	0.342

[1] Liquid Petrolatum, Specific Gravity = 0.8873.

V. The Interfacial Tension of Emulsifying Agents:

These lower the interfacial tension so greatly, that the correction for specific gravity becomes less important. The corrected values are shown in Table V, for liquid petrolatum, olive oil, and air.

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[1] Harkins and Humphrey: J. Am. Chem. Soc. 38, 242, (1916).

TABLE V

The Interfacial and Surface Tension of Colloidal Emulsifying Agents

Solution	Conc. percent	IFT (corrected) Liq. Pet.	IFT (corrected) Olive Oil	Surface Tension Air
Soap	1.0	*	*	0.342
Soap	0.1	0.171	0.335	**
Bile Salts[1]	0.5	0.194	0.333	0.531
Bile Salts	0.1	0.349	0.564	0.693
Saponin[2]	0.5	0.893	0.725	0.903
Saponin	0.1	**	0.729	**
Tannin	5	0.684	0.634	0.896
Tannin	1.	0.832	0.871	0.951
(Sucrose	4.3	0.986	0.911	1.007)

[1] Bilein-Abbott Laboratories.
[2] Quillaja saponin, Merck.
*Drops too rapid to count.
** Not tried.

It is seen that even tannin, which is a rather inefficient emulsifier, lowers the interfacial tension materially and to about an equal degree toward petrolatum and olive oil; the effect increasing, but not proportionately, with the concentration. It has relatively little effect on the air surface.

Saponin acts markedly on the olive oil surface, independently of concentration. The petrolatum and air surfaces are distinctly, but relatively little affected.

Bile-salts and soap lower the tension at all surfaces to the greatest extent; the effect increasing with concentration, but not proportionately. The lowering is greatest toward liquid petrolatum, least toward air.

Summarizing these changes, it appears that soap, bile-salts, saponin, and tannin lower the interfacial tension toward air, liquid petrolatum and olive oil, the efficiency being in the order named.

The efficiency is generally of a comparable magnitude toward the three media; the petrolatum interface being however relatively susceptible to bile salts and soap; the olive oil interface relatively susceptible to saponin; and the air interface relatively less susceptible to all.

Saponin appears to have the peculiarity that the effect does not increase materially with the concentration.

VI. Alkali or Interfacial Tension of Fatty Oils.

The formation of soap, especially in oils containing free fatty acid, must lower the surface tension very greatly. Illustrative of this are the corrected interfacial tension values calculated from the data of Donnan[1] shown in Table VI.

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[1] Z. physik Chem. 31, 42, (1899).

TABLE VI

Effect of Alkali on the Interfacial Tension of Rape-Seed Oil[1]

Molecular Concentration of Sodium Carbonate	Interfacial Tension (corrected)
0.0005	0.615
0.00075	0.497
0.00100	0.367
0.00150	0.184

[1] Not purified to remove the fatty acid.

Conclusions

1. In determining interfacial tensions, it is necessary to apply a correction for specific gravity.

2. The interfacial tension with this correction may be expressed by the formula:

$$\text{IFT} = \frac{\text{drops W}}{\text{drops S}} \times \frac{\text{grav.S} - \text{grav.Oil}}{\text{grav.W} - \text{grav.Oil.}}$$

(*IFT* stands for corrected interfacial tension, relative to water = 1; *Drops W* = number of drops formed in water; *drops S* = number of drops formed in the solution; *grav. S* = specific gravity of the solution; and *grav. oil* = specific gravity of the oil; and *grav. W* = specific gravity of water, i.e. 1.000.

3. When the proper correction for specific gravity is applied, the effects of solutions of the salts of the Hofmeister series (in M/8 concentration) toward liquid petrolatum fall within the experimental error of the Donnan pipette. With olive oil the changes are also very small, except when an alkaline reaction leads to the formation of soaps.

4. Of organic substances, the effects of sugar and urea toward liquid petrolatum also fall practically within the experimental error; but glycerol lowers the interfacial tension distinctly, and chloral and especially alcohol very markedly. This is perhaps connected with their lipoid solution affinity.

5. Colloidal emulsifying agents (soap, bile-salts, saponin, tannin) lower the interfacial tension toward liquid petrolatum, olive oil and air. The efficiency is very high for soap, and decreases in the order named. The change is of a similar order of magnitude for the three media.

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THE SUPERHEATING OF LIQUIDS

BY FRANK B. KENRICK, C. S. GILBERT AND K. L. WISMER

When a liquid is heated in an open tube it is generally possible to raise the temperature above its boiling point without ebullition taking place. But both the extent to which the superheating of a given liquid can be carried and also the length of time for which a liquid may be kept superheated at a given temperature vary in an apparently quite capricious way from experiment to experiment. No satisfactory explanation has been given for these phenomena, and indeed there are few definite facts known on which an explanation can be based. In this research an attempt is being made to obtain some definite information concerning these phenomena.

The superheating of liquids[1] and the closely allied phenomena of the "stretching of liquids"[2] and the supersaturation of gases[3] have been the subject of comparatively few investigations, while on crystallization of supercooled liquids and solutions[4] countless papers have been published.

Two methods of investigation have been followed: (A) suddenly heating the liquid in open capillary tubes at atmospheric pressure[5] and (B) reducing the pressure on the liquid in closed tubes at fixed temperature[6].

A. Heating Liquids in Open Capillary Tubes

Apparatus. In ordinary test tubes and in many capillaries there are definite points on the walls which cause bubbling. Everyone has seen streams of bubbles rising persistently from the same spot in the side of the tube, and sometimes when a liquid is superheated in a straight capillary tube, part of the liquid jumps out leaving the same amount in the tube several times running. In order to reduce the chance of the presence of these obvious imperfections in the walls very small capillary tubes were used. To facilitate filling and to eliminate the sealed end the capillaries were bent into narrow U-tubes about 10 cm. high. For temperatures above 200°, at which soft glass was rapidly attacked by water, Pyrex glass was used. For lower temperatures and for non-aqueous liquids soft soda glass was employed. The tubing from which the capillaries were drawn was cleaned with chromic acid cleaning mixture, dried, and kept sealed till required. When a test was to be made a tube was opened and a portion heated and drawn out to a capillary from 1 to 0.3 mm. inside diameter and from 0.2 to 0.07 mm. wall thickness.

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[1] J. Meyer: Nernst Festschrift, 278 (1912); Kenrick: Trans. Am. Electrochem. Soc. 23, 425 (1913); Wismer: Trans. Roy. Soc. Can. 15, 49 (1921).

[2] Berthelot: Ann. Chim, 30, 232 (1850); Worthington, Phil. Trans, 183, 355, (1892); Dixon: Proc. Roy. Soc. Dublin (2) 12, 60 (1909).

[3] Wismer: Trans. Roy. Soc. Can. 16, 271 (1922). See also next article.

[4] One of the most recent: Hinschelwood and Hartley: Phil. Mag. 43, 78 (1922).

[5] A summary of some of the results obtained by this method by C. S. Gilbert was published in Trans. Roy. Soc. Can. 15, 53, (1921).

[6] By K. L. Wismer in 1922.

A convenient set of constant temperature baths consisted of a number of tin cans fitted with reflux condensers and containing liquids of various boiling points. Into the top of each can was soldered a brass thimble about 5 cm. deep containing Russian petroleum.

Method. A freshly made capillary U-tube was filled with the liquid by suction. It was then plunged suddenly, about 4 cm deep, into the temperature bath and the time noted on a stop-watch before explosion took place. To find roughly the time required to heat the liquid in the capillary to the temperature of the bath a similar-sized straight capillary tube closed at the bottom and drawn to a very fine thread at the upper end was filled with nitrobenzene and used as a thermometer. It was found that in three seconds the nitrobenzene had expanded practically to its limit. That the superheating observed was not in any way affected by possible cooling by convection currents was concluded from the fact that the same superheating was observed in tubes in which the lower part of the U was bent into a horizontal position. Also similar results were obtained when very long U-tubes, filled to the top with liquid, were employed, in which case cooling by evaporation from the surface would be impossible.

Results. As a result of hundreds of preliminary experiments it was quite obvious that freshly heated capillary tubes were much more favourable to superheating than tubes which had been long exposed to the air. This result is analogous to the fact that a freshly heated thread of glass may be dipped into a glass of soda water without causing effervescence, while after a few minutes exposure to the air, or after being touched with the finger, it causes immediate evolution of carbon dioxide.

With freshly prepared or freshly heated capillaries it soon became evident that, in spite of a persistent capriciousness in the results, there were certain general regularities of behavior. The most striking result was the very rapid shortening of the time interval, before explosion, with rise of temperature. Ether, for example, was frequently kept for over an hour at 100°, while at 140° it was never possible to keep it more than a few seconds, and yet at this temperature the vapour pressure is not much more than twice that at 100°.

Secondly, experiments showed that whatever the effects of heating may be it is not cumulative in the sense that the effect of heating and cooling repeatedly without explosion has any noticeable influence on the result of subsequent heating. For example, a tube of ether was heated to 115° for five seconds and cooled for five seconds 20 times without explosion. On continuous heating it then exploded in 35 seconds.

A third general result follows from a comparison of the present experiments with those described by Wismer[1]. This comparison shows that the same relation exists between temperature and supersaturation whether the liquid is suddenly raised to a high temperature at atmospheric pressure or whether at high temperature and high pressure, the pressure is suddenly reduced to atmospheric pressure.

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[1] J. Phys. Chem. 26, 301 (1922).

In spite of these general conclusions, however, which are the result of a great many observations, it is quite apparent that there is not even an approximate constancy in the time interval between heating and explosion even with the same tube, at the same temperature, and with liquid taken from the same sample of material. For example, a tube was filled with ether, placed in an oil bath at 122° and the time noted before explosion. The tube was refilled and the experiment repeated 20 times. The interval of time between the moment of immersing and the explosion varied quite irregularly from 2 to 75 seconds, but 15 of the experiments lasted less than 30 seconds. The same tube, which it is presumed would go on behaving in a similar irregular way, and for which the probability of it lasting for more than 30 seconds was not great, was again filled and heated. If the ether exploded in less than 30 seconds it was refilled, but if it lasted 30 seconds it was taken out of the bath and let cool for a few seconds, put back in the bath, and again if it lasted 30 seconds, let cool, etc. Of four fillings which lasted more than 30 seconds one exploded on the second reheating, one lasted for three reheatings, one for 14 and one for 16 reheatings. The general irregularity of the intervals makes it seem unlikely that the explosions were caused by any one particular imperfection in the glass, while the persistence[1] with which some of the fillings which had outlived the 30 seconds could be re-heated for this period seems to show that either (a) these particular samples of ether were different from the majority, or (b) a particular condition of the walls existed in those cases, which however might be altered completely by the shock of an explosion. The results are certainly not in accord with the assumption that the initiation of the bubble depends *entirely* on some property of the liquid itself in which there is an element of chance.

An attempt was made to decide between these two possibilities by making definite changes in the treatment and material of the capillary tubes and in the nature and purity of the liquid used. The results are disappointing in so far as none of the changes tried led to any increase in the tendency of the liquids to superheat above that shown in the ordinary freshly heated capillaries, or to any decrease in the capriciousness of the time interval.

Changes in the tubes. (1) Various kinds of glass were used for the capillaries. No difference could be established in the behaviour of Pyrex, soda glass and clear quartz.

(2) Metal capillaries were less favourable to superheating than glass: glass silvered by ammoniacal silver nitrate and tartrate was probably less favourable than unsilvered glass.

Tube	Liquid	Temp.	Average time before explosion
Glass	ether	126	5 sec.
Glass silvered	"	120	3 "
Brass	"	60	2 "
Steel	"	60	2 "

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[1] A result to a certain extent contradictory to this is recorded in Part B of this paper.

(3) As already stated, exposure of the tubes to air for some time is unfavorable to superheating.

(4) Evacuation of tubes at high temperature. (a) A long capillary tube bent into a flat spiral was immersed in boiling mercury for an hour while the pressure in the tube was kept down to less than 1 mm. It was then sealed off, cooled, the tip broken off under freshly boiled ether, and the whole cut up into a number of U-tubes. (b) A similar set of tubes was prepared by evacuating and heating in an airbath till some of the tubes collapsed. (c) A similar set was evacuated to a pressure of 0.001 mm and heated for an hour to the temperature of boiling sulphur. Although the last set appeared to favour superheating somewhat more than the others none of the tubes behaved decisively differently from the ordinary freshly drawn capillaries.

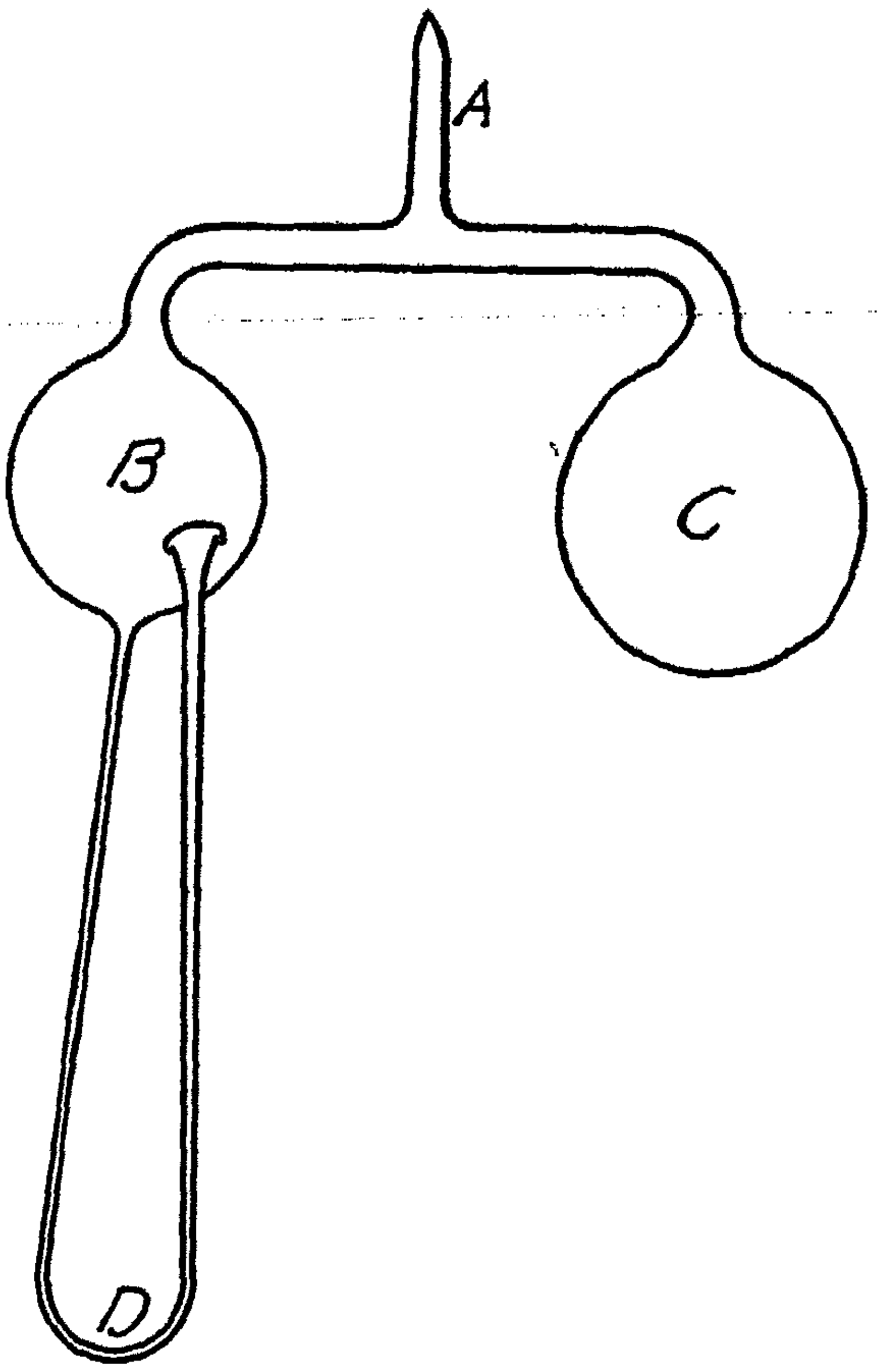

Fig. 1

Tube	Liquid	Temp.	Average time before explosion
Freshly drawn	ether	126	5
Treatment (a)	"	127	3.4
Treatment (b)	"	127	4
Treatment (c)	"	133	4

Among the last set was one capillary which after being refilled and exploded five times stayed at 143° for 2 seconds. This was the highest temperature ever reached in open capillaries with ether.

(5) Capillary tubes digested for two weeks in Russian petroleum, with alternate heating to 150° and cooling, and subsequently washed with ether were less favorable to superheating.

(6) Capillary tubes washed out rapidly with hydrofluoric acid, then with water, and dried in a current of hot air, were, if anything, less favourable to superheating of ether than before treatment.

Changes in the liquid. (1) One of the most obvious assumptions to account for the differences in the behaviour of different samples of liquid is that the motes which are present in all ordinary liquids initiate the bubbles. In order to test this assumption mote-free ether was prepared in the apparatus shown in Fig. 1[1]. Three distillations were made in vacuo without ebullition from bulb *C* to bulb *B*, and between each distillation, during the rinsing back, care was taken to cause a rapid current to flow five or six times through *D*. The liquid in *C* was found to be quite mote-free on examination with an intense beam from an arc-light. Tube *D* was then immersed in an oil bath at 127.6° and the times noted before explosion. The intervals were: 7 sec, 80 sec; the third time it did not explode till five minutes and it then broke the tube, but it is thought that in the last test there was a difference in level in the bulb which caused a current through the capillary. In a new apparatus at a temperature of 130.5° explosion took place in eight tests in from 1 to 3 seconds after immersion. From these experiments it would appear that motes in the body of the liquid are not an important factor in the initiation of bubbles, although to be certain of this result a much larger number of tubes, *D*, would have to be tried.

(2) Addition of colloids. The presence of starch, colloidal platinum[2], and argyrol hindered superheating. An old solution of colloidal silica had apparently no effect. Pyrex tubes were used:

Liquid	Temp.	Average time before explosion
water	240°	8 sec
Water+3% starch boiled	153	6 "
Water+0.1% argyrol	169°	7 "
Water+0.02% colloidal platinum	135°	2 "
Water+colloidal silica prepared 13 years ago	236°	5 "

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[1] See Martin: J. Phys. Chem. 24, 481 (1920) and Kenrick: J. Phys. Chem. 26, 73 (1922).

[2] See also next article, p. 1310.

(3) Addition of soluble substances. Small additions of soluble substances to water had little or no effect.

Liquid	Temp.	Average time before explosion
Water+ 4 % aniline	236	6 sec
Water+2.7 % amyl alcohol	238	8 "
Water+0.6 % sulphuric acid	213	3 "
Water+6.5 % sulphuric acid	238	3 "

The results are surprising. It is commonly thought that solutions of sulphuric acid are more liable to "bump" than pure water. This is very likely the case in ordinary vessels.

Although it was generally impossible to superheat ether in tubes previously washed out with water and imperfectly dried, a solution of ether and 0.6% water held at 117° for over 5 seconds seven times running.

(4) A number of pure liquids were investigated to find the maximum temperatures to which they could be heated without explosion. In these tests a capillary of liquid was dipped into an adjustable oil bath at a temperature about 40° above the boiling point of the liquid. If the liquid did not explode in 10 seconds the capillary was removed while the temperature was slowly raised about 2° per minute. Every 10 seconds a test was made until an explosion occurred. Then another capillary was filled and started about 30° below the last explosion point and the temperature slowly raised as before. As the previous explosion point was neared the time the tube was kept in the bath was decreased to 5 seconds. The following table gives the highest temperatures reached in this way, together with the vapour pressures corresponding to these temperatures, and the boiling points of the liquids. For the last three columns see "Discussion of Results," p. 1305).

TABLE I

Liquid	Highest Temp. t_m	Corresponding vapor press. p_v	Boiling point	Action to glass	γ_{t_m}	$r \times 10^7$
Ethyl ether	143	11,500	35	Contact angle	3.5	4.5
Ethyl alcohol	201	22,700	78	Wets	3.88	2.5
Methyl alcohol	180	20,100	66		6.41	4.7
Chloroform	173	11,000	61			
Acetone	174	14,400	56			
Carbon bisulphide	168	11,700	46	Contact angle		
Water	270	41,200	100	Wets	20(?)	7.3
Sulphur dioxide	50	6,300	−10			
Benzene	203	11,200	79	Contact angle	6.88	9.2
Chlorbenzene	250	8,300	132		8.04	16.7
Brombenzene	261	6,100	156			
Aniline	262	———	183			
m-Xylol	235	———	137			

(5) Although in all the above experiments the liquids were always thoroughly boiled just before use, to "drive out the air," we have never been able to convince ourselves that this precaution made the slightest difference in the superheating. It no doubt helps the vessel in which the boiling takes place, and this probably is the reason for the prevalence of the opinion that liquids must be free of air in order to be successfully superheated.

B. Reducing Pressure on Liquids in Closed Tubes at Constant Temperature

From the results already obtained it seems likely that either the walls of the vessel or nuclei attached to the walls are one of the causes of the variability of behaviour of liquids on superheating. It is also not unlikely that both in the method just described and in the pressure method reported on previously[1] the shock of the explosion resulted in variations in the conditions under which each successive bubble formation took place. In order to minimize the effect of this shock and also to aid in locating the origin of the explosion the following method was adopted. Ether was used in all the experiments.

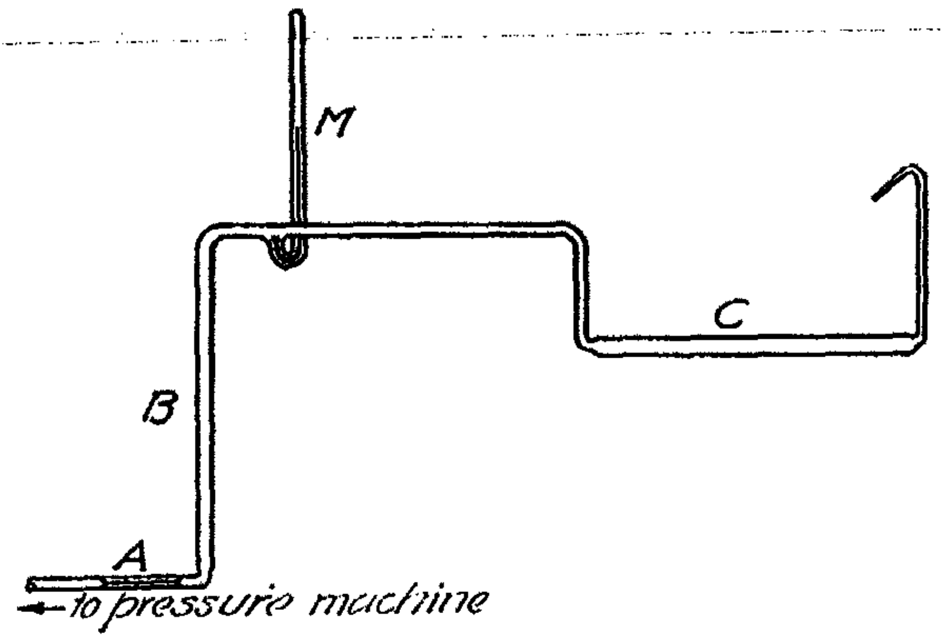

FIG. 2

Apparatus. In Fig. 2, the ether to be superheated is contained in a small tube *C*, 10 cm long, outside diameter about 2.5 mm, which is connected by a very fine capillary to a minute mercury-air manometer and a vertical tube *B*, 12 cm. long by 2.5 mm diameter. Another short piece of fine capillary *A* connects the apparatus to a screw pressure machine. The whole apparatus was filled with ether, twice distilled over sodium, and boiled immediately before use. The ether was subjected to about 20 atmospheres pressure and the bulb immersed in an oil bath at 125°. A few trials of reducing the pressure to one atmosphere showed a probability of a time period sufficiently long to effect a seal-off at *A*, and after a number of attempts in which the explosion occurred in the middle of the operation, a successful seal was made at atmospheric pressure.

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[1] Wismer: J. Phys. Chem. 26, 301 (1922).

Method. We now have a tube full of liquid at 125° and at atmospheric pressure in which the bubble of vapour formed cannot grow very large. The vapour may again be liquefied by the compression brought about by warming *B* in a beaker of hot water. The great compressibility of hot ether allows the attainment of this pressure without seriously endangering the apparatus by even considerably over-stepping the required compression. The bubble formed on explosion was about 5 mm long. After compression and condensation of the bubble the pressure can be brought to 1 atmosphere again in from 4 to 5 seconds.

Results. The bulb *C* was put in the oil-bath at 124.6°–124.7°, and the pressure reduced by cooling *B*. The time was noted from the instant the manometer indicated atmospheric pressure until the explosion occurred. The following time periods for one set of experiments give a very good indication of the wide variation in results, (time in seconds): 165, 105, 145, 90, 60, 250, 75, 240, 500, 270. Many similar experiments were carried out.

(1) It was found that the bubble did not start at the point where it had previously disappeared.

(2) In only two instances, out of over 40 experiments did a bubble appear at the same spot on three or four consecutive explosions. Often two or more bubbles appeared simultaneously and in one case as many as eight appeared distributed along the tube. Since in spite of efforts to keep the bubble as small as possible it could not be prevented from growing to 4 or 5 mm in length, only the region in which the bubble occurred could be noted and not any well-defined point.

(3) It was thought that if there were obtained a time interval considerably above the average it might indicate that a condition of the tube existed which was more favourable to superheating than in previous instances, and that the pressure might be applied and reduced a number of times with long time intervals without explosion. The results, however, do not lead to such a conclusion. The average time for which ether could be held without explosion at atmospheric pressure and at 130.5 was 60 seconds for the particular tube used in the apparatus; if no explosion occurred in 120 seconds pressure was again applied, held for two minutes and reduced a second time. On each second trial the explosion always occurred after a very short interval, much shorter than the average. The results may be illustrated by one set of experiments; in which the first ten tests were used to find the average time interval, (time in seconds):

At 130.5° bubble formed after 160, 25, 45, 65, 10, 75, 60, 13, 40, 43, (Average = 59), 120 no bubble; (applied pressure for 2 minutes) bubble formed after 20, 25, 40, 80, 25, 120, no bubble, (applied pressure for 2 minutes), bubble formed after 33, 25, 7, 90, no bubble, (applied pressure for 1 minute), bubble formed after 15.

This result appears to be contradictory to those recorded on page 1299 from the experiments with open capillaries. It should be noted, however, that the conditions are different in the two cases in several respects. The open tubes had been violently agitated by explosions every few moments, while after the long time intervals the only disturbance consisted in spontaneous cooling. In the present case no violent agitation occurred, but after each long time interval a very considerable pressure was applied.

(4) One set of experiments was carried out at 130.7° after a long heating of over three hours above 120°. The average time period obtained in this set was 119 seconds, as compared with an average of 67 seconds for a set previously performed at the same temperature but without the long heating.

(5) A test was made in which the pressure was reduced for 30 second intervals and applied for 30 second intervals. In three cases the totalled time period was 115 secs. 155 secs. and 93 secs., while the average time for 18 explosions was 98 secs. in which one of the tests held for 350 secs. This is in accord with the result with open tubes (page 1298).

(6) A small tube similar to *C* Fig. 2, was attached to the pressure machine, filled with ether, and immersed in the thermostat. On slowly reducing the pressure the ether always exploded at one point before atmospheric pressure was reached. The tube was removed from the bath, rested on a heavy glass tube which was tapped, thus making the small tube vibrate violently. When the tube was then returned to the bath there were found to be two other spots at which an explosion was as likely to take place as at the former spot.

Discussion of Results. The difference between different capillaries, the absence of favourable effect on superheating of the removal of motes, and the great extent of the irregularities of the results make it seem likely that the initiation of the bubble is not due mainly to a lack of uniformity in the body of the liquid, either in respect to the liquid itself or to motes in the liquid.

The difference in the behavior of the same tube from one experiment to another, and the persistence with which some fillings which were not allowed to explode could be held repeatedly, suggest that there are differences in the walls of the tube which are affected by each explosion. Such behavior might be explained by the action of motes attached loosely to the walls of the tubes[1].

That adsorbed or occluded gases are not an important factor in starting bubbles in freshly heated tubes is shown by the experiments with exhausted and baked capillaries. It is possible however that such gases are of influence in unheated tubes or tubes which have been exposed long to the air.

If any process is occurring between the moment of raising the temperature or reducing the pressure and the moment of explosion it must be a reversible process, for there is no indication that heating and cooling without explosion affect the likelihood of the subsequent explosion.

The capriciousness of the experiments with closed tubes in which the disturbance caused by the bubble formation might be expected to be slight

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[1] That there is an apparently inexhaustible supply of detachable motes at the surface of glass vessels which are not removed in the preparation of mote-free water by distillation in vacuo has been proved by Mr. Garrard in this laboratory.

point to the existence of a chance factor in addition to the irregularities at the walls of the tubes, unless the great pressure increase due to the formation of the bubble is also sufficiently disturbing to entirely alter the walls between each experiment.

The rather definite upper temperature limit is very puzzling. It is not clear from the experiments whether there is a real limit or merely a very rapid shortening of the time period with rise of temperature. If the radius, r, be calculated for a vapour bubble which can exist in equilibrium with the liquid at the maximum temperature reached, t_m, the values shown in the last column of Table I are obtained. In the calculation it was assumed that

$$r = \frac{2\gamma}{1.36 \times 980 \times p_v} \text{ cm}$$

where γ is the surface tension in dynes/cm and p_v is the vapour pressure in millimetres at the maximum temperature The values of r are of the same order of magnitude, but there are differences which can hardly be accounted for by the uncertainty in the determination of the highest temperatures. To change r for ether, for instance, from 5.1μμ to 3.2μμ would require a change of temperature from 140 to 150. A reason, moreover, for attaching some importance to the values, r, is that for the same liquid (ether) the change in maximum temperature with the external pressure p_m fits in very well with a constant value for r over a very wide range, as pointed out in Wismer's work[1]. Thus if r be taken as 4.5×10^{-7} cm the following external pressures p_m, expressed in atmospheres, are calculated for the maximum temperatures, t_m by the formula

$$p_m = \frac{p_v}{760} - \frac{2\gamma}{1.36 \times 980 \times r} + 1$$

TABLE II

maximum temp. t_m	γ	p_v	external pressure, p_m in atmospheres
180°	0.64	21780mm	26.8
160°	2.08	15730	12.6
140°	3.77	11030	− 1.0
20°	16.49	42	−72

In 20 determinations made at pressures varying from 1 to 25 atmospheres the maximum temperatures maintained for an appreciable time differed in 19 cases by less than 2° from the values calculated from the above formula, and in one experiment by less than 4°. And in the one case on record of the "stretching" of ether[2] at room temperature the minimum pressure reached was −72 atmospheres.

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[1] J. Phys. Chem. 26, 306, (1922).

[2] Meyer: Zur Kenntnis des negativen Druckes in Flüssigkeiten (1911).

However, the increase in vapour pressure and decrease in surface tension with rise of temperature are not sufficient to account for the extraordinarily rapid shortening of the time interval with rise of temperature. The assumption of local fluctuations in the density of fluids which in recent years has afforded such a convenient concept for expressing many of the properties of liquids may possibly be found suitable in the present case, for if a definite fluctuation of density, involving a quantity of material determined by r is required to initiate a bubble the probability of the event happening would increase rapidly with the decrease in r.

If nuclei on the glass are the origin of bubble formation, one would expect differences in effectiveness depending on the ability of the liquid to wet the material of the nucleus. In this connection it is worth noting that of the organic liquids for which information is available[1] (see fifth column, Table I), ethyl alcohol ($r=2.5\times10^{-7}$), is the only one which wets glass without a contact angle. Water, it is true, also wets glass, but its exceptional behaviour ($r=7.3\times10^{-7}$) may be due to its action on the glass at high temperatures. There is an apparent connection between the association coefficient of the liquids and the pressures in col. 3, Table I, though a reason for this is not obvious.

Summary. 1. Experiments have been made on the superheating of liquids by heating the liquids in open capillary tubes at atmospheric pressure and by reducing the pressure on the liquids in closed tubes at constant temperature. Temperatures have been reached, at atmospheric pressure, from 50° to 170° above the boiling points of the liquids.

2. The initiation of bubbles in freshly drawn capillary tubes appears to be connected with nuclei loosely attached to the walls of the vessels and with a property of the liquid in which there is an element of chance.

3. In freshly drawn capillaries neither dissolved gases in the liquid nor, apparently, adsorbed gases on the glass are important factors in initiating bubbles.

4. The radius of bubbles which could exist in equilibrium with the liquids at the highest temperatures to which they can be superheated varies from 2.5 to 16$\mu\mu$.

5. There is a simple relation between the external pressure and the maximum temperature attainable which holds over a very wide range of pressure.

Chemical Department,
University of Toronto,
June 11, 1924.

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[1] Miss Pockels: Physik Zeit. **15**, 39, (1914).

SUPERSATURATION OF GASES IN LIQUIDS

BY FRANK B. KENRICK, K. L. WISMER AND K. S. WYATT

The work described in this paper was begun some years ago and part of it has already been reported in abstract[1]. Although it is not yet completed the recent appearance of an article under the same title[2] makes it inadvisable further to delay publication of the details.

In most of the previous work on supersaturation the phenomenon has probably been complicated by one or more of three factors: (1) crystalline form of the separating substance, (2) effect of the walls of the containing vessel, (3) dust particles suspended in the liquid. We have avoided the first difficulty by using gases. The effect of the vessel walls has been eliminated to a certain extent in the present work, and it is hoped later to be able to employ dust free liquids prepared by some of the methods already worked out in this laboratory.

The work may be taken up under three heads: (A) Solutions made by shaking water and the gas under pressure, (B) Supersaturated solutions prepared by chemical formation of dissolved gas, (C) Ultra-microscopic investigation of capillary tubes of solution under pressure.

A. Solutions made by shaking Water and the Gas

Before giving the details of the experiments it may be well to quote the conclusions already reached in the work by Wismer[3].

"Solutions of oxygen and of carbon dioxide were investigated at atmospheric pressure at concentrations corresponding to pressures up to about 50 atmospheres in the case of oxygen and 35 in the case of carbon dioxide. The results obtained up to the present seem to justify the following conclusions:

1. A long heating of tube and solution at high temperature was found to favour supersaturation.
2. The time interval between the reduction of pressure and appearance of a bubble varies between wide limits even under apparently identical conditions.
3. Suspended particles (e.g. colloidal platinum) introduced into the liquid rapidly lose their effectiveness in starting the bubbles.
4. It is almost certain that in all cases the bubbles were initiated at the surface of the glass, although the location on the surface was by no means constant except in tubes in which there were obviously imperfections in the glass.
5. Although carbon dioxide is nearly thirty times as soluble as oxygen, the average time interval before formation of bubbles is about the same for

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[1] K. L. Wismer: Trans. Roy. Soc. Canada (3) 16, 217 (1922).

[2] J. Metschl: J. Phys. Chem. 28, 417 (1924).

[3] Loc. cit. This has not yet been reviewed in Chemical Abstracts.

the two gases at the same temperature when the supersaturation corresponds to the same equilibrium pressure.

6. On the assumption that the bubble originates from a spherical particle acting as a nucleus which the bubble just encloses, the diameter of such a particle was calculated to be at most 5×10^{-7}cm*".

Method and Apparatus. The difficulty encountered with the ether in preventing the growth of large bubbles (see preceding article) is almost wholly overcome in experiments with a supersaturated solution of gas in water. In this case the formation of a bubble of gas in the liquid depletes the immediate neighborhood of dissolved gas, and the bubble must grow by the diffusion of gas from a more concentrated portion of the liquid. Hence the bubble grows comparatively slowly and there is no violent reaction to disturb the rest of the liquid.

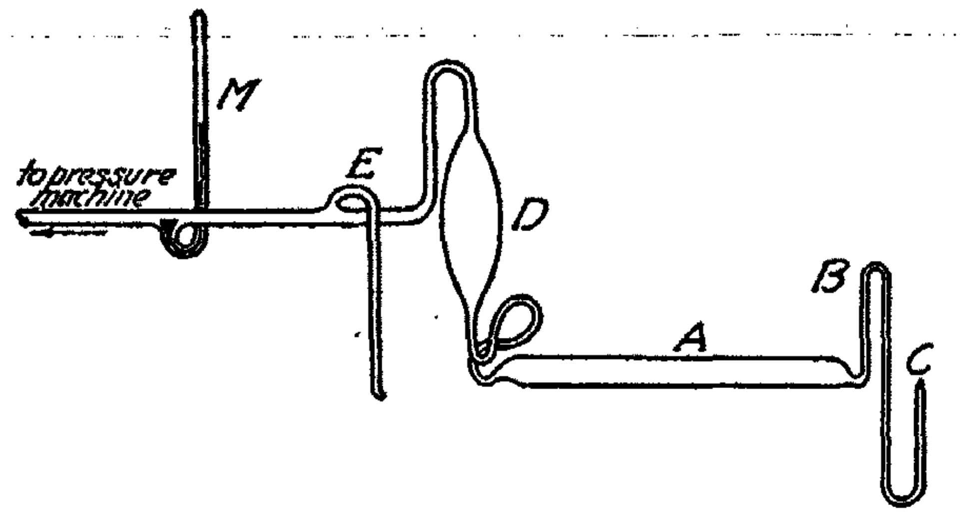

Fig. 1

Oxygen and carbon dioxide were chosen for study, as examples of slightly soluble and very soluble gases. The oxygen used was the commercial gas from a cylinder; the carbon dioxide was made in a Kipp apparatus from marble and hydrochloric acid.

The form of apparatus used is shown in Fig. 1. The tube, *A*, 60 mm × 6 mm inside diameter, contains the supersaturated liquid. *D* is a bulb large enough to hold the contents of *A*. *E* and *BC* are capillary tubes used for filling the apparatus. The small manometer *M* is used to indicate atmospheric pressure. The whole is made of well-annealed soft glass of a suitable thickness to stand over 50 atmospheres pressure.

The apparatus is first filled with water. The open tip, *C*, is then brought up under a test tube of oxygen inverted in a dish of water. By unscrewing the screw of the pressure machine the liquid in *A* is drawn back into *D*, and is followed by oxygen. A little water is then drawn in to fill the tube *BC*, and the tip *C* sealed off. By applying a pressure of from 30 to 40 atmospheres the gas is compressed to a small bubble. A motor-driven mechanical arrangement slowly raises and lowers the apparatus through about 30 cm. by means of a string attached to a wheel on the ceiling. The apparatus is attached to

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* This is wrong. This was the number for superheated ether put in here through error. The value should have been 23×10^{-7}.

the pressure machine and hydraulic pressure gauge by a horizontal flexible glass capillary about a meter long, and the gas bubble is thus made to run from end to end in tube *A*. Even with this arrangement an hour or more is necessary to effect solution. When the gas is all dissolved the pressure is reduced to one atmosphere, the tip *C* broken off and a fresh supply of gas drawn in. The operation may be repeated many times until the desired concentration is reached. The equilibrium pressure of the gas in solution was found by dissolving all but a minute bubble and then adjusting the pressure until the bubble was seen to grow neither smaller nor larger on measurement every three minutes with a microscope provided with an etched micrometer scale. On complete solution the pressure was, of course, increased by a slight but almost negligible amount.

Results. (1) An amount of oxygen equal to approximately half the volume of *A* was drawn into the tube and dissolved under 30 or 40 atmospheres pressure, giving a solution whose equilibrium pressure was about 16 atmospheres. With this concentration of gas bubbles did not appear on reducing the pressure to one atmosphere, at room temperature, even after an hour, and it was found necessary to heat the tube to the neighborhood of 60 or 70° to obtain bubbles within a reasonable time.

(2) Experiments were performed which had another advantage over those with superheated ether, namely, that after the formation of one bubble time could be allowed for the formation of one or two more bubbles. The following record is typical of a number of experiments. Different portions along the length of the tube may be represented by *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h*. The equilibrium pressure of the oxygen was 16 atmospheres. At 61° and 1 atmosphere a bubble appeared in 4 seconds at *a*; one second later another bubble appeared at *e*; 10 seconds later no more bubbles had appeared and pressure was applied to redissolve the gas. At 58° and 1 atmosphere a bubble appeared in 75 sec. at *g*; 10 seconds later another at *a*; 20 seconds later another at *d*.

(3) The effect of temperature on the time interval for which a liquid can remain at one atmosphere is shown very strikingly by one tube whose time intervals in the neighborhood of 80° varied from 10 seconds to 4 minutes. This tube at room temperature gave rise to a bubble only after more than 76 hours, although at this temperature the absorption coefficient of oxygen is scarcely twice as great as that at 80°.

(4) One tube was filled with a solution of colloidal platinum which had been prepared by Bredig's method some months before, and from which all the larger particles had settled out. Oxygen equal to about half the volume of the tube was dissolved in it giving an equilibrium pressure of about 16 atmospheres. On the first reduction of pressure to one atmosphere at room temperature 9 bubbles appeared almost simultaneously after two seconds. These were dissolved, and a second time 9 bubbles appeared after three seconds. On a third trial 3 bubbles appeared in three seconds, and no more appeared in the next 40 seconds. A fourth reduction of pressure gave no

bubbles in 11 minutes, and pressure was again applied. Thus the effectiveness of the colloidal platinum in starting bubbles is rapidly lost.

(5) One tube, in which a concentration of oxygen corresponding to an equilibrium pressure of 30 atmospheres at 20° had been built up, held for 75 seconds at 72° at atmospheric pressure, without formation of bubbles. (No doubt much higher concentrations could have been obtained for shorter time intervals.) From Winkler's solubility values[1] for oxygen at different temperatures, and assuming Henry's law the equilibrium pressure at 72° was calculated to be 51.5 atmospheres. The radius r of a bubble which could exist in equilibrium with the liquid under those conditions would be 23×10^{-7} cm. If the maximum supersaturation of oxygen attainable be calculated on the basis of $r = 7.3 \times 10^{-7}$ (the value obtained for water from superheating experiments; see preceding article) a concentration is found corresponding to a pressure of 202 atmospheres at 20° and 168 atmospheres at 72°.

(6) A few experiments were made with carbon dioxide in water. Since the absorption coefficient of this gas at room temperature is 0.878[2] a great many fillings were necessary to build up a high equilibrium pressure. After 14 fillings of the tube the pressure was found to be 9 atmospheres; after 24 fillings the pressure was 14 atmospheres. At room temperature and at 40° a bubble did not form in 10 minutes. It was necessary to raise the temperature to from 55° to 70° before bubbles would form in ten minute intervals. The capriciousness of the behaviour is very similar to that of the oxygen solutions. In one test it was possible to keep the liquid at atmospheric pressure at 79° for 15 seconds. The equilibrium pressure was again determined at the conclusion of the experiments and found to be 12 atmospheres, the loss being due to slow diffusion through the capillary connecting A and D. Using an extrapolated value for the absorption coefficient at 79° and assuming Henry's law, which is not strictly true for carbon dioxide, an equilibrium pressure of over 35 atmospheres was calculated.

B. Supersaturated Solutions prepared by Chemical Formation of the Gas

Method and Apparatus. Highly concentrated solutions of nitrogen were prepared by warming, under pressure, solutions in which dissolved nitrogen is produced by chemical reaction. Fig. 2 gives a diagrammatic representation of the apparatus. A is a screw pressure machine from which the 100 atmosphere hydraulic gauge used in part A has been removed. This is connected by a small copper tube to the needle side of a needle valve. The seating side is connected by similar tubing to a sealing wax joint and thence by glass capillary tubing to the thick-walled glass bulb B of about 5cc. capacity, in which is the meniscus between the oil of the press and the water used in the rest of the system. The air-filled manometer whose lower half was made from 0.9 mm and upper half from 0.3 mm tubing was of such dimensions

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[1] Ber. 24, 3602 (1891).

[2] Seidell: "Solubilities of Inorganic and Organic Compounds."

that at 200 atmospheres the mercury stood about 20 mm from the top. This was joined by a loop *E* of about two metres of capillary glass tubing (about 2 mm outside and 0.7 mm inside) to a T-piece made of very small tubing, the lower end of which led to the solution vessel *F*, 8 mm outside diameter and 10 cm long with about 1.5 mm wall thickness. This vessel was painted black with the exception of four narrow vertical slits where the paint was scraped off as shown in the sectional view, Fig. 2. The tubes *C* were used for filling the system and for blowing into when making sealed joints or repairs.

The apparatus was always tested to 200 atmospheres before beginning an experiment. It may be worth noting that most of the breakages consisted in the bursting of *F* and in the splitting of T-pieces. It was originally intended to heat *F* to 70°, keeping the lower end cooled to prevent bubbles forming at the bottom, but we never succeeded in getting a tube to stand the pressure under this condition, although Pyrex, lead glass, and Jena glass were tried in addition to soft soda glass which was found to be the best. All tubes were made as small as possible. The only T-pieces that could be relied upon were made very carefully from tubing about 3 mm outside diameter and 1 mm bore. The advantage of thick glass walls was apparently more than offset by the difficulty of avoiding strains in the glass-blowing.

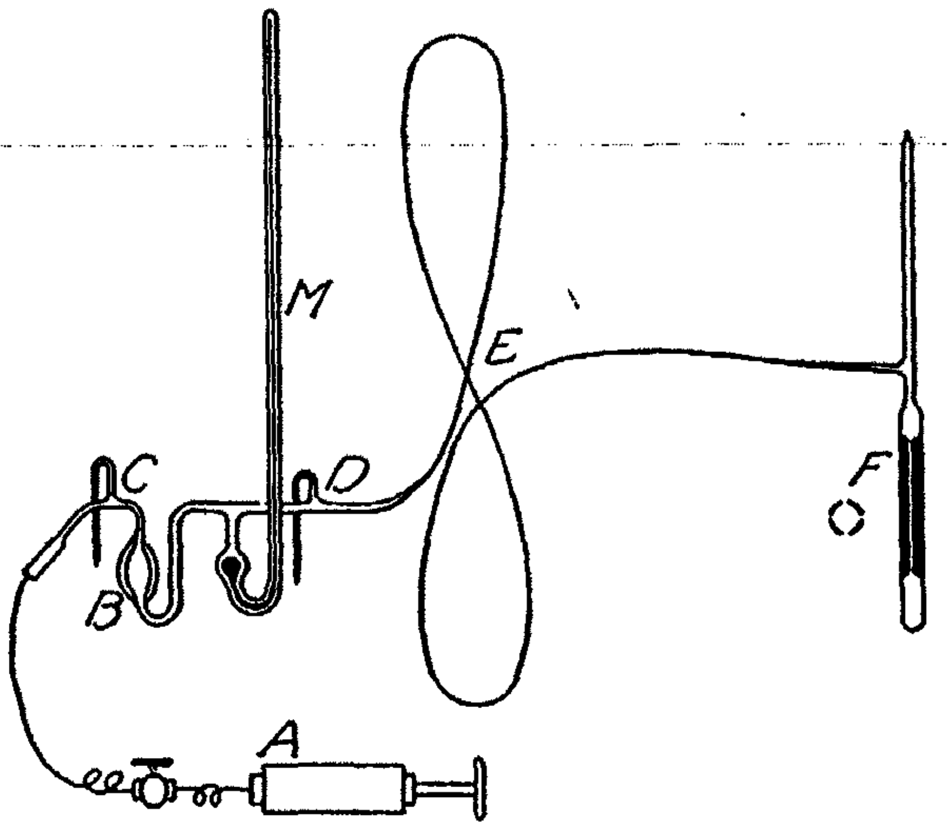

Fig. 2

The method of procedure was in general as follows. Dissolved nitrogen was generated in a warmed aqueous solution in the vessel *F* while the pressure was maintained at a value sufficient to prevent bubbles forming, until the reaction was complete. The time necessary for this was found by blank experiments in test tubes with fine rubber delivery tubes, the gas from which was measured by collecting over water. In these blank experiments the solution, temperature, and duration were the same as in the actual experiments, but in the blanks the tubes were shaken vigorously every few minutes to cause evolution of the gas. As the reactions used might safely be assumed to be non-reversible, the fact that the gas was evolved in one case and not in the other could not affect the quantity, and would be very unlikely to affect the rate of formation of the nitrogen. When the reaction was complete the tube *A* was allowed to cool to the room temperature. There is now in the tube a solution which, when the pressure is reduced to 1 atmosphere will be very highly supersaturated.

A beam of light from an arc lamp was then passed through the tube from right to left and observation was made through the front slit by means of a lens. With this method of illumination bubbles rising from the sides of the vessel, although visible by light reflected inside the tube could be easily distinguished from bubbles rising through the middle of the tube which shone out like sparks. Bubbles rising from the bottom could be distinguished from bubbles formed in the body of the liquid by the fact that the former could not come into view near the top of the tube till a couple of seconds after the pressure was reduced.

There are not many reactions suitable for producing the gas. The reaction must be slow enough to give time for thorough mixing, for filling the tube through a fine capillary, and for sealing up the tube; and fast enough to be complete in a reasonable time, for the needle valve was never so tight that the apparatus could be left overnight at 150 atmospheres without a fall of 20 or 30 atmospheres. Also it was not possible to heat the tube to above 70° without greatly increasing the risk of it bursting, and as it generally broke even at room temperature there was not much to come and go on. Many trials were made with ammonium chloride and sodium nitrite mixtures containing various acids. Acetic acid worked fairly well, but so much of it had to be added that the results obtained were inconclusive on account of the probably great increase it causes in the solubility of nitrogen. Finally the reaction between hydrazine sulphate, ferric alum and sulphuric acid was found to be exactly what was needed.

Results. Only two successful experiments have been made as yet. A description of one will suffice to show the nature of the result. 3cc of a solution containing about 6 percent hydrazine sulphate were mixed with 6cc of a solution containing, per 100cc, about 8 g. conc. sulphuric acid and 40 g. hydrated ferric alum. This was run quickly into the vessel *A*. Then a few drops of water were added to rinse out the top of the capillary and make a clean seal possible. The tip was then closed and the pressure raised to 150 atmospheres. A beaker of water surrounding *A* was next slowly raised to 60° and kept at that temperature for 30 minutes and finally allowed to cool to room temperature. Finally after adjusting the lantern and the necessary screens etc., the pressure was suddenly lowered to 1 atmosphere. Bubbles rose from the sides and bottom immediately but none from the body of the liquid.

It is not possible to determine the equilibrium pressure from the quantities of material used, since the effect of the various dissolved substances on the solubility of nitrogen is not known, but the following facts give information.

Two or three times during the cooling of the tube the pressure inadvertently fell to about 100 atmospheres and a stream of very minute bubbles was seen slowly rising from a point near the bottom of the tube. This stream could be stopped by screwing the pressure up to 125 atmospheres. This, of course, does not show that the equilibrium pressure is between 100 and 125 atmospheres, but it shows that it must be at least 100 atmospheres. It is clear therefore that a liquid with a concentration of nitrogen corresponding to over 100 atmospheres can be brought to atmospheric pressure for an appreciable time without bubbles forming in the body of the liquid. As stated in Part *A* one might expect supersaturation corresponding to 200 atmospheres to be about the limit that could be reached in glass vessels with walls free from imperfections. Unfortunately this pressure is so near the breaking point of the apparatus that we have not yet succeeded in determining whether bubbles form in the body of the liquid with this degree of supersaturation. To settle this our apparatus will have to be very considerably modified.

C. Ultra-Microscopic Investigation of Capillary Tubes

In these experiments which are as yet quite incomplete, mixtures of hydrazine sulphate and ferric alum similar to those used in Part B are drawn into a very fine flattened capillary tube sealed horizontally to the pressure system just described. The mixture however in these experiments was coloured red by addition of a little ammonium sulphocyanate solution in order to make it easier to be sure it was in the tube. The tip of the capillary was then sealed off, the pressure raised and a dish of water kept at 60° brought up round the capillary for 30 minutes. After that the tube was cooled and dried and the microscope slid into position. The cover-glass, below which was the cedar oil in which the capillary was immersed, was supported on two little rods slightly thicker than the capillary, so that the microscope could be slid backwards and forwards to examine different parts of the tube, and could be slid completely away if it was necessary to heat the tube again or refill it. When the pressure is lowered the growth of the bubbles can be observed and it is hoped by this method to locate their position in reference to the motes visible on the surface of the glass. Although no breakages have occurred in the flattened capillary repeated accidents to other parts of the apparatus have prevented the completion of more than two experiments. In the first in which the concentration of nitrogen corresponded to about 70 atmospheres, no gas bubbles appeared at all even after more than five minutes, which confirms and extends the result recorded in Part A. In the second, in which a stronger mixture was used bubbles had already formed when the tube was examined, though there were still long stretches of capillary with no bubbles. This result, however, is not free from objection for if the bubbles were formed before reduction of pressure this would cause considerable stirring of the liquid and the intermediate parts of the liquid might have lost nitrogen.

Summary

1. Experiments have been made with water supersaturated with oxygen, carbon dioxide and nitrogen.

2. Liquids have been saturated with gases at concentrations corresponding to pressures of over 100 atmospheres and the pressure has been reduced to one atmosphere without bubbles forming in the body of the liquid. Liquids containing gases at concentrations corresponding to nearly 100 atmospheres have been reduced to 1 atmosphere without bubbles forming even on the walls.

3. As in the case of superheating of liquids there is, with rise in temperature, a very rapid shortening of the time interval between the lowering of pressure and formation of bubbles, in spite of the fact that the absorption coefficient of the gas decreases but little with rise of temperature.

4. Colloidal platinum in solutions supersaturated with oxygen is favourable to the formation of bubbles, but it rapidly loses its effectiveness.

5. A long heating of the tube containing the solution at a high pressure was found to favour supersaturation.

6. Although carbon dioxide is nearly 30 times as soluble as oxygen the average time interval before bubble formation is about the same for the two gases, at the same temperature, when the supersaturation corresponds to the same equilibrium pressure.

Chemical Department,
University of Toronto,
June 14th, 1924.

ON THE REACTIVITY OF SOLID PHASES[1]

BY J. ARVID HEDVALL

A.

A Survey of Earlier Works

In every chemical reaction it is a necessary condition that the particles, which are going to form new molecules, possess some degree of mobility. When two substances, the particles of which can form a chemical compound, are mixed together as a powder, there is such a comparatively thick layer of gas or such a small contact-surface between two adjacent grains, that the chemical attraction is generally not able to act. But even if the layer of gas is removed, or the contact otherwise is made better, the forces of affinity will have much difficulty in forming the compound in question, because they must overcome the forces, which hold the particles bound at definite points of the space-lattices. Even in mixtures where this is possible, the compound produced will in most cases very soon prevent the continuation of the chemical process by covering the grains with impermeable films. It is accordingly not surprising that chemists of the past century set up the rule: *Corpora non agunt nisi fluida.* Towards the end of the past century however, chemists had accustomed themselves to look upon matter and its transformations in agreement with the kinetic theory. Thus it became evident, that a sort of mobility must be attributed even to the particles of solids. At certain points they are able to leave their normal ranges of oscillation and move over into the range of attraction of other particles, either of the same crystal or of such an adjacent substance producing diffusion or formation of compounds.

Faraday, working with iron and platinum, was the first really to show, that layers of alloys are slowly formed even at comparatively low temperatures, when pieces of the metals were pressed together. After him many other relevant observations have been made, of which the classical experiments by Roberts-Austen,[2] on the rate of diffusion between gold and lead, ought to be mentioned. He observed, that already at 100°C after 30 days the gold had diffused against gravity in amount easily determinable. During the decades of 1880 and 1890 W. Spring[3] published a number of papers on the same phenomenon, as well in metallic systems as in other mixtures. Working with very high pressures he showed, that the increased contact-zone contained small quantities of the reaction product formed. He also attributed

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[1] This paper contains a survey of the author's *partly* published results relating to his investigations in connection with these matters from about 1912 up to the present time. The author has however found it expedient to begin with a short summary of the earlier most important results in this line, being the basis upon which he has tried to continue building.

[2] Proc. Roy. Soc. 59, 283 (1896).

[3] Bull. Acad. Roy. Belg. and Z. physik. Chem.

to the pressure a certain influence on the reaction, facilitating the formation of those reaction-products which possess a smaller molecular volume than the original substances. This point of view has also been of great importance to the comprehension of the formation of secondary minerals in pressed rocks.

At the end of the past century a new auxiliary science—metallography—began to be abstracted from physics and chemistry. By means of suitable furnaces, thermoelements and microscopes the method of thermal analysis, elaborated by Tammann, showed the prevalence of changes in solid metallic systems.[1] A great number of investigators have shown later, that reactions of each of the following three classes occur with sufficient rapidity to be easily observed and objectively studied; in many cases however the reaction heat is too small to make itself visibly felt on the heating curves:

1. On cooling, some solid solutions can form such solutions of another composition, e.g. the system Cu-Zn. The diagram shows two gaps[2] of concentration for the Cu-Zn-mixed crystals. One of them runs between 30-37% Zn at 910°C. At 400°C this interval is displaced to 37-45% Zn, the solubility of Zn in the mixed crystals, which are rich in Cu, having namely been increased by lowering the temperature.

2. A change of a solid solution can take place, when one of the components suffers allotropic modifications, e.g. the Fe-C-system,[3] where on the cooling- and heating-curves discontinuities appear, corresponding to the transition-points of iron at 1410°, 890° and 770°C.

3. A chemical compound can be formed or decomposed, e.g. in the system: Mg-Sb.[4] On the heating-curves the temperature rise already at 280°C begins to be accelerated, corresponding to the formation of $Mg_3 Sb_2$. This temperature is 310°C below the lowest eutectic point.

The phenomena, which in the literature have been brought together as *recrystallisation*[5] also prove, that solids must not be looked upon as entirely stereotyped structures. At normal temperature however the mobility of the particles is generally far too small to enable the formation of compounds or solid solutions in a reasonable time, a fact already appearing from the research made by Roberts-Austen. Further, Masing,[6] carefully examining the results of Spring, showed that mixtures of metal-powders which have been pressed together at very high pressures, contained no other substances than the original ones, when the mixture had not been heated. Thus he found for instance, that mixtures of Bi and Tl powders, having been compressed at 5000 atm., at normal temperature first showed after about *one year* the blue contact film of mixed crystals, which was visibly formed in five *hours* at 120°C. In most mixtures the temperature must be still further

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[1] cf. any treatise on Metallography and Desch: Report on Diffusion in Solids, Brit. Assoc. Adv. Sci. (1912).

[2] Shepherd: J. Phys. Chem. 8, 421 (1904).

[3] cf. any treatise on Metallography.

[4] Masing: Z. anorg. Chem. 62, 279 (1909).

[5] Masing: Die Naturwissenschaften, 1923, 413.

[6] Z. anorg. Chem. 62, 265 (1909).

raised before any noticeable quantity of the reaction-product is formed. But there are indeed also examples which prove, that in some cases the mobility of the particles even at normal temperature is sufficient to bring about changes in the mixtures. We know for example that the recrystallization of Sn begins already at 45°C.[1] In order to give an idea of the change of the diffusion of metals into each other by increasing the temperature the following determinations of their diffusion-coefficients may be mentioned.

Au in Pb[2]	Au in Ag[3]
100°C: 0.00002 cm^2/day	870°C: 0.000037 $\frac{cm^2}{day}$
165°C: 0.004 "	
200°C: 0.7 "	

At constant temperature (475°C) Weiss and Henry[4] measured the thickness of the diffusion zone between pieces of Ag and Sb, which were pressed together various times:

after	2 hours	0,38 mm.
"	12 "	0.98 "
"	72 "	2.15 "
"	360 "	4.90 "

With the exception of these transformations in metallic systems and the very slowly occurring imitations of mineral changes in stiff magmas[5], there is very little known about chemical changes between solid phases. Before describing the most characteristic cases of real chemical reactions of this sort, which were known up to about the beginning of the second decade of this century, it may be mentioned, that solid solutions or mixed-crystals have been produced also in non-metallic systems. Bruni and Meneghini[6], for instance, succeeded in the formation of KCl – NaCl mixed-crystals of the same properties, as if they had been produced by melting and freezing. They heated these sort of mixtures above 400°C, but below the eutectic point 654°C of this system. The rate of diffusion became observable at about 500°C. Other relevant observations have also been made in other systems of inorganic *salts* and organic substances after the classical work of van't Hoff[7]. The interesting investigations on the electric conductivity of solid solutions may be cited, especially as they have also been of great practical importance. Fritsche[8] dealing with oxides and haloid-salts, observed in 1897, that the electrical conductivity of these compounds was at low temperatures, very small if the compounds were entirely pure. But small quantities of those substances;

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[1] cf. Masing: Naturwissenschaften, loc. cit.

[2] Roberts-Austen: loc. cit.

[3] Franckel and Heuten: Z. anorg. Chem. **116,** 1, (1921).

[4] Compt. rend. **174,** 1421 (1922).

[5] cf. Liesegang: "Geolog. Diffusionen" (1913) and Endell: N. Jahrb. d. Mineralogie, Geologie (1913): II, 129.

[6] Atti. acc. instit. sci. Veneto **1911-12:** II, 195.

[7] Z. physik. Chem. **5,** 322 (1890).

[8] Wied. Ann. **60,** 300.

with which solid solutions can be formed, are able considerably to increase the electrical conductivity. At a certain temperature it increased from value 2 for pure PbF_2 to 8000 for a solid solution of 2% KF in PbF_2. Similar results have been obtained with the solid solutions of those oxides of the rare earths which are used in the Nernst lamp.[1]

The first real chemical reactions between solid non-metallic phases, which were methodically studied, are described by Spring[2] 1884 and 1885. The most typical results of his works concerning this subject may here be mentioned. Proceeding from the knowledge, that the soluble sulphides are very easily formed, Spring pressed together at 6500 atm. powders of such metals and sulphur, took the mixture out of the press, crushed, ground, pressed once more and so on. Thus he found, for example, that a compressed piece of Ag and S contained after one, two, four and six consequent pressings respectively 4, 51; 12, 43; 46, 74 and 69, 4% Ag_2S. In this as well as in other relevant series it is striking, that the quantity of the reaction product is smallest after the first compression. Probably the subsequent grindings have given a finer powder than in the original mixture. The great importance of the impermeable films, which must have been found round the grains by the reaction substance, appears from the following data. An analysed mixture of Cu and S contained after the first compression of 8,49% CuS and after being ground and compressed once more 16,95%. Another time the same mixture with 8,49% CuS remained in the press for four years. The analysis gave hardly 4% more CuS than in the mixture, twice compressed and ground. Each compression seems to have lasted a few hours. In this way Spring produced a great number of sulphides, arsenides and tellurides. One further experiment may be mentioned.[3] He pressed together at 6000 atm. very finely ground, carefully desiccated mixtures, partly

of 1 $BaSO_4+3\ Na_2CO_3$ and partly
of 1 $BaCO_3+3\ Na_2SO_4$

His results appear from the following table, where the progress of reaction is indicated in % of the theor. complete process.

	Number of compressions		a few hrs.	7 days	14 days	21 days	28 days
$BaSO_4+$ $+3No_2CO_3$	1	6000 atm.	0,94	1,60	3,08	3,94	3,84
	3	6000 "	4,78	6,78	9,01	—.	9,15
	6	6000 "	8,99	9,94	10,89	—.	11,08
$BaCO_3+$ $+3No_2SO_4$	1	6000 "	59,16	63,91	64,66	—.	— —
	3	6000 "	69,25	74,98	77,38	—.	— —
	6	6000 "	73,31	80,68	80,31	—.	— —

The reaction-process thus approaches in both cases a state of equilibrium. One fact however makes it problematical, whether the reactions really occur without influence of a liquid phase. Repeating the experiment at 120° he

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[1] cf. Reynolds: Dissert. Gottingen (1902).
[2] Bull. 41, 492.
[3] Bull. 44, 166; 46, 299.

found that the quantities of the reaction-products were smaller. This makes it possible that the Na_2CO_3 and Na_2SO_4 during the repeated grindings and mixings have absorbed moisture from the air.

The chemistry of silicates brought the next advance after Spring, as to the reactions in solid mixtures of inorganic compounds: Cobb[1], 1910, studied the reactivity in mixtures of $CaCO_3$ and SiO_2 at various temperatures. He found the following quantities of $CaSiO_3$ formed in % of the theoretically complete reaction.

After	28	hours	at	800°C	2,5%
"	1	"	"	1100°C	5,8%
"	1	"	"	1200°C	14,4%

Similar results were also obtained in various mixtures of CaO, Na_2O, Al_2O_3 and SiO_2. He always found that the temperature exerted a much greater influence than the time, just as also was stated in the metallic systems and generally also in the mixtures investigated by Spring. Cobb did not however go the whole way, explaining these phenomena as real reactions between solid phases. Instead of this a "quasi vaporous film" of the reacting substances was assumed. Similar results were also obtained by Endell[2] on heating mixtures of MgO, ZnO and BaO with SiO_2 or Al_2O_3.—In analogy with the researches of the phenomena of recrystallization in metals cited such investigations have been made and with analogous results in systems of inorganic salts.[3]

From the historical summary we have seen, that this branch of chemistry is still in the period of its very first growth. We can at least partly explain this as follows: It is evident, that the investigators in the first place directed their attention to the mechanism of the reactions in homogeneous systems, when a claim to a deeper comprehension of those phenomena began to make itself felt. We know, that these problems have been of a sort, that has entirely absorbed all the great work, that has been placed at it disposal. We also know, that first in recent time we became able—and still very imperfectly—to survey the conditions in systems, where *one* solid phase is reacting with liquid or gaseous phases. In consideration of this, that the real and necessary foundation for a rational penetration of the mechanism of reacting solid phases was laid first by the splendid works of v. Laue and of W. H. Bragg and W. L. Bragg. We are, however, still very far from mastering reactions of this sort in such a manner as in the homogeneous systems. Dealing with the solid state of matter we have to pay regard to many important factors as transition-points, size of the grains, impermeable films and so on. But even when the influence of all these and many other factors is cleared up, we shall not be able completely to survey these phenomena, before our mathematical physicists and crystallographers have learned to know the particulars of the conditions of oscillation in the space-lattices. Till that

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[1] J. Soc. Chem. Ind. 69, 250, 335, 399, 608, 799 (1910).

[2] Z. angew. Chem. 1913, 582.

[3] cf. Rinne and Boeke: Min. petrogr. Mitt. 27, 393 (1908).

time chemists have to produce and systematize the necessary material.—The last few years have already given us a very great number of extraordinarily interesting results in this line. Thus, through the joint work of mathematicians, physicists and crystalllographers and chemists, a beginning has been already made in laying a solid foundation, upon which the future chemistry of solid phases will be built. It would however carry us too far to give here a survey of these works, which are still somewhat hard briefly to summarise and to judge from this point of view.

B.

A Survey of the Author's Results

In the following pages I have summarized some characteristic examples of my experiments during ten years study of the reactivity of matter in the solid state.

In a few words they can be summed up as follows:

I. An application of thermal analysis is able to give very reliable information of eventual reactions also in pulverulent non-metallic mixtures.

II. Many oxides of metals have proved to be very reactive substances in forming not only solid solutions, but also compounds with each other at comparatively low temperatures and often at a surprising rate.

III. In many cases the temperature of thermal dissociation ($p = 760$ mm.) can be easily determined.

IV. The influence of the magnitude and form of the grains and of the "prevention films" on the reaction process has been observed and preliminarily studied.

V. The obvious difference in chemical and physical properties, that very often can be observed for a great number of metal oxides according to their various methods of preparation follows from a different crystallographical development of the surface, but not from different space-lattices. These were unaltered in spite of very different methods of preparation of the oxides. In cases, where really different modifications exist, their different reactivity can be shown with help of heating-curves.

VI. Many reactions, which occur with astonishing intensity have been found, and preliminarily studied, in mixtures of peroxides with oxides or other peroxides.

VII. A new class of reaction between solid phases:

$$\mathrm{MeO + MAc = MeAc + MO + Q};$$

has been discovered. MeO and MO are metal-oxides of which MeO must be more basic than MO. MAc and MeAc are salts of an oxygen acid, and Q is the heat of reaction.

I

When heating a solid, in which neither chemical reactions nor any change of state takes place, the heating-curve will run without discontinuities, being a logarithmic one. But this regular form disappears, when the heating involves any sort of molecular change. Changes, corresponding to an absorption of heat, appear on the curves as arrests, whilst reactions, which are accompanied by a development of heat, will be indicated by the curves suddenly ascending more steeply. In demonstrating the properties of alloys, this method has for a long time already been generally used. Without having been really tried, the method however was looked upon as quite impossible for pulverulent non-metallic mixtures, because of their small conductivity of heat and above all because it was assumed that the rate of the reaction was too inconsiderable. Taking precautions however, as follows, we shall find, that the heating-curves, which are erected by observing the thermoelement every 10 seconds, very truly record the changes in the mixtures.

The thermoelement must be placed in the centre of the mixture, and the quantity of the powder must be adjusted to the kind of reaction in question. The heating must be gradual and regular. In a system, where the reaction occurs accompanied by a *great* reaction-heat, the initial temperature—i.e. the temperature, corresponding to the visible beginning of the reaction—would be noted too low, when the mixture was rapidly heated, and this value would be still further lowered by taking a greater quantity of the reaction-powder. In mixtures, where the reaction is accompanied by a *smaller* reaction-heat, these factors are of less importance. Accordingly in studying the reactions:[1]

a) $BaO+CaSO_4=BaSO_4+CaO+46$ kgcal.

b) $BaO+SrSO_4=BaSO_4+SrO+11$ kgcal.

the following initial temperatures (t)° were observed:

a)		16°C per 10 sec.	6°C per 10 sec.	3°C per 10 sec.
	t=	354°C	360°C	370°C
b)		20°C per 10 sec.	12°C per 10 sec.	4°C per 10 sec.
	t=	368°C	369°C	372°C

Taking about 0,2 gr. of the reaction-mixture and heating with a rate of from 1 to 3°C per 10 sec. the initial temperatures recorded will however agree very well with each other. In cases of *very small* reaction-heats (about under 5 kgcal/mol.) it may sometimes be necessary to take a greater quantity of the powder or to press a pastil in order to increase the contact between the two components. The effect on the curve can also in such cases sometimes be increased by joining another reaction to the original one, for instance[2]

$$MgO+CoSO_4=MgSO_4+CoO+1{,}5 \text{ kgcal.}$$

This small reaction-heat does not make itself felt on the heating curve, but when the reaction is allowed to occur in oxygen, the secondary reaction: $CoO+\frac{1}{6}O_2=\frac{1}{3}Co_3O_4+21$ kgcal. occurs, accompanied by a considerable development of heat.

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[1] cf. Z. anorg. Chem. 128, 4 (1923). (together with Heuberger).

[2] loc. cit.

II[1]

Mixing powders of CoO (Co_3O_4 or $CoCO_3$) and ZnO in order to investigate the chemical character of Rinman's green", it was found that the green substance was very rapidly formed by heating the powder at about 800°C. The analysis showed, that the substance was to be regarded as mixed-crystals of a zincate of CoO and ZnO. The known examples of such mixed-crystals between metal oxides, being at that time (1912) very rare, the investigation was extended to other reactions between CoO, or NiO, and other metal oxides. In many cases an unexpected rate of the reaction was observed. (Later (cf. VI. and VII.) reactions between solid phases of extraordinarily greater rate were found). Heating the mixtures at about 800°C chemical compounds as well as mixed-crystals were formed in a few minutes to a surprisingly great percentage, even without stirring the mixture. Mixed-crystals were formed of CoO with MgO, ZnO (CoO · ZnO), MnO and NiO; and of NiO with MgO ZnO (NiO · ZnO), Mno and CoO. A very great number of compounds were observed, of which only the following became isolated:

$CoO \cdot Al_2O_3$, $\cdot 4\ CoO \cdot 3\ Al_2O_3$, $CoO \cdot Cr_2O_3$, $2CoO \cdot SnO_2$, $CoO \cdot To_2O_5$; $NiO \cdot Al_2O_3$; $\cdot 2NiO \cdot SnO_2$; $CuO \cdot Al_2O_3$.[2]

III

With the help of this method of heating-curves we are able to take a rapid survey of the conditions of the thermal dissociation of a chemical compound. In many cases we are also in this very convenient manner able to determine exactly the dissociation-temperature corresponding to a certain pressure—for inst. one atm. The dissociation generally occurs more rapidly and at a lower temperature the more volatile the acid anhydrous oxide is and the less positive the basic oxide is. Thus for instance, $CaCO_3$ dissociates at a much greater rate and at a lower temperature than $CaSO_4$ and $BaCO_3$. The heating-curves of $CaCO_3$ show perfectly horizontal arrests at 918°C,[3] corresponding to a CO_2-pressure of 760 mm. The corresponding temperatures of $CaSO_4$ and $BaCO_3$ are $>1060°$ and about 1360°C.[4] Another example of such a determination is presented by the reaction:

$$CO_3O_4 = 3CoO + \frac{1}{2}\ O_2 \text{ at } 912°C\ (p_{c_2} = 1\ \text{atm.})^5$$

A sharp determination of an equilibrium temperature of this kind is of course only possible in those cases where the dissociation occurs rapidly giving perfectly horizontal arrests on the heating-curve. The precautions, mentioned in I and II must of course be followed.

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[1] cf. the author's dissertation: Über Reaktionsprod. von CcO mit anderen Metalloxyden. Upsala (1915 and Z. anorg. Chem. 86, 201; (1914); 86, 296 (1914); 92, 301 (1915); 92, 369 (1915); 92, 381 (1915); 93, 313 (1915); 103, 250 (1918).

[2] together with Heuberger: Z. anorg. Chem. 116, 137 (1921).

[3] Z. anorg. Chem. 98, 47, (1916).

[4] Z. anorg. Chem. 128, 7, (1923).

[5] Z. anorg. Chem. 96, 64, (1916).

There are however some more facts, which we must consider, in determining these temperatures and especially of course, when we are going to fix a real equilibrium temperature. These factors are mentioned in IV.

IV

a). The Magnitude and Form of the Grains

By the rate of a reaction[1] we mean the number of molecules of the reaction product formed per unit of time. Regarding this, the rate of a reaction must depend upon the contact-surface of the components and consequently be the greater the smaller the average diameter of the grains. This means, that the minimum rate of a reaction, necessary for its observation, will, in fine-grained mixtures, be arrived at—and be consequently indicated on the heating-curves—at a lower temperature than in a coarser grained mixture. This appears very obviously from the following table.[2]

Kind of reacting substance	Reaction	Observed temperature
Co_3O_4, made of pyrophorous CoO, oxidized by the air. An extremely fine-grained, light brown, loose powder.	$Co_3O_4 = 3CoO + \frac{1}{2}O_2$	912°C.
Co_3O_4 made by heating $CoCO_3$ at 450°C. The product is darker and less fine-grained than the former.		922°C.[5]
Co_3O_4, made by heating $Co(NO_3)_2$ at 450°C. The powder is black and coarse grained.		952°C.[5]

Accordingly a laminated powder also will prove more reactive than one of equally developed grains. As to the solubility of a solid substance in acids, this could be very obviously shown by comparing the decidedly laminated Fe_2O_3, which is made by heating any sulphate of Fe, with a Fe_2O_3 preparation of any other origin. The latter are all more or less spherical and accordingly of a less development of surface. This spherical, inactive sort of Fe_2O_3 can also be obtained from the "sulphide-oxide" by heating it above about 1000°C. The effect of the heating involves a change of the form of the grains, the laminae gradually becoming spherical.[3] The influence of this heat-shrinking in diminishing the reactivity can also be demonstrated as to solid phases and their reactions. Thus the horizontal intervals of the heating-curves on heating of the following Co_3O_4—preparations were found to be the higher the longer the substance was heated:

$$Co_3O_4 \rightleftarrows 3CoO + \frac{1}{2}O_2$$[4]

Co_3O_4 heated in N_2 at 800°C about 15 min.: $t = 946°C$.[5]

Co_3O_4 heated in N_2 at 800°C about 30 min.: $t = 959°C$.

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[1] The isothermal reaction rate is of course otherwise defined.

[2] These temperatures are of course not equilibrium temperatures.

[3] Z. anorg. Chem. **121**, 217, (1922).

[4] Z. anorg. Chem. **96**, 68, (1916).

[5] These temperatures are of course not equilibrium-temperatures.

A similar change of the reactivity of Co_3O_4 with Al_2O_3 in the formation of $CoO \cdot Al_2O_3$ could also be observed.[1]—Thus it is evident, that the visible beginning of a reaction not only depends upon the quantity of the substance in question and the manner in which it is heated (cf. p. 1324), but also upon the form and magnitude of the grains, which have a great influence upon the reactivity.[2] Taking precautions in regard to the first two factors as is mentioned above and working with powder-mixtures, which have been even ground in an agate-motar, the several determinations will however differ very little from each other, i.e. we are able to obtain results capable of being reproduced. No other *general* rules can be laid down for investigations of this sort. Every special case generally requires its particular precautions, and these will easily be found after the construction of a couple of heating curves.

b) When heating such mixtures, it is however impossible to obtain a complete reaction. A smaller or greater quantity of the components will be left after the first heating and will react first after being once more ground and mixed. The second amount of the formed reaction product is smaller than the first one and so on. Accordingly on the corresponding heating-curves a still smaller effect will be observed, but it is however generally indicated on the second and in cases of great reaction-heat even on the third and fourth curve.

These observations prove very clearly, that the reaction is brought to a stand-still owing to impermeable films of the reaction-product, which are formed between the reacting grains. When the mixture is ground once more, these films will be destroyed and a contact between the reacting components will be formed afresh. In systems, where the reacting occurs at a very great rate, e.g.[2] $BaO+CuSO_4=BaSO_4+CuO+68,4$ cal, it seems however as if the "prevention-films" in question will not have time enough to form impenetrable layers. When heating this mixture, reactions up to about 88% occurred in a fraction of a second. In mixtures however, where the reaction occurs more slowly, they are of greater importance. Already the reaction:[3]

$$CaO+CuSO_4=CaSO_4+CuO+22,4 \text{ kgcal.}$$

gave after the first heating only 60% reaction-product and after grinding and mixing once more 70%. When heating extremely slowly (about 0,1° per 10 sec.) a system, in which the reaction occurs comparatively slowly, (which besides is possible only in systems of small reaction-heat) the temperature of the beginning of the reaction may be invisible on the heating-curve, being however clearly visible at normal heating-rate (1-3° per 10 sec.). Heating so very slowly the reaction begins and continues very slowly, and, accordingly the reaction-product will have time enough to form a more and more thick and coherent layer between the grains. Thus the reaction in this manner is already brought to an end by a very small and slowly formed quantity of the reaction product.

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[1] Z. anorg. Chem. 96, 71, (1916).
[2] cf a later study of Hinshelwood and Bowen: Phil. Mag. 1920, 569.
[3] Z. anorg. Chem. 128, 9 (1923).

The various reactivities of the different states of modification of a solid can also be studied in the same way, the sudden increase of the temperature of the heating-curves at the reaction-temperature being much greater for an unstable modification than for a stable one. The following example may be mentioned.[1] Two mixtures were made; the one of $CaO+$amorphous SiO_2 and the other of $CaO+$christobalite. The first was heated up to 1350°C and the other up to 1410°C. The amorphous SiO_2 had thereby reacted to 6,9% and the crystallized to 0,6. Similar results were also obtained in other systems.

The known different properties—also the reactivity, following from different manners of preparation—of a number of metal oxides investigated do not however depend upon any difference in the state of the modification, but only upon the development of surface as above described. With the help of the method of Debye and Scherrer it was shown that the space-lattices of these metal oxides were the same in spite of a great number of different methods of production. For instance, 27 different preparations of Fe_2O_3 gave an identical X-ray-diagram.[2]

VI

Reactions of great intensity have been observed on heating mixtures of a peroxide of the alkaline earths with other oxides. Up to now these reactions are however only superficially described.[3] On heating BaO_2 together with one of 35 oxides examined, generally a very intense reaction sets in, accompanied by an active development of oxygen from the BaO_2, at a temperature some hundred degrees below the dissociation temperature of BaO_2, which is about 800°C at 760 mm. In cases, where the oxide can be oxidized, e.g. Cu_2O,MnO,MnO_2 and Cr_2O_3 such a development of oxygen however was not observed, if the mixture had been made in agreement with the corresponding formulae:

$$BaO_2+Cu_2O=2CuO+BaO.$$
$$2BaO_2+MnO=BaMnO_4+BaO.$$
$$BaO_2+MnO_2=BaMnO_4.$$
$$3BaO_2+Cr_2O_3=2BaCrO_4+BaO.$$

Every oxide, that is an anhydrous acid oxide, in the existing or any higher degree of atomicity, reacts with BaO_2 forming a salt. Only three oxides were totally inactive: SnO,SnO_2 and ZrO_2. The reactions between BaO_2 and other oxides, e.g. MgO,CaO,CuO,CdO are harder to understand. The development of oxygen at relatively low temperatures gives the impression of a catalytical decomposition. Neither these reactions nor the reaction of SiO_2[4] with BaO_2 can however be looked upon as catalytic phenomena, assuming 800°C to be the dissociation temperature of BaO_2 (760 mm.). It is

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[1] Z. anorg. Chem. **98**, 57 (1916).

[2] Z. anorg. Chem. **120**, 327 (1922).

[3] Z. anorg. Chem. **108**, 119 (1919), (together with N. v. Zweighbergk). The reaction temperatures, noted in this paper are all too low, because we were not at that time conscious of the great importance of the rate of heating. (cf. p. 1322).

[4] Z. anorg. Chem. **104**, 163 (1918).

necessary to assume, that a real reaction between the two oxides takes place, forming an unstable intermediate product, which afterwards easily decomposes.

Something like that may also occur on heating mixtures of the peroxides with each other. The astonishing intensity of these reactions can in some cases be of an almost explosive character. A compound of such an intermediate kind, that afterwards decomposes extremely rapidly, is e.g. indicated in mixtures of BaO_2 and Na_2O_2, where something like a fulmination takes place, only if the mixture is prepared after the following molecular proportion: $3BaO_2+Na_2O_2$.

My purpose is, of course, to investigate these reactions more closely.

VII

It seems that specially great interest ought to be ascribed to that new class of reactions, the first examples of which are published in two earlier papers under the title: "Transference of Acid Between Solid Phases." [1]

In general we can characterise these reactions as follows (cf. pag. 1321):

1. A reaction takes place, when Q means a development of heat.

2) The intensity of the reaction is the greater, the greater Q is.

3) The reaction temperature is higher the less basic the oxide (MeO) is. BaO accordingly reacts at a lower temperature than SrO and SrO lower than CaO. (As to the influence of the salt cf. below.)

4) The mechanism of the reactions cannot be explained by assuming a gaseous phase of the anhydrous acid.

5) The baking-together of the mixture after the reaction is a pure result of the reaction; the harder the mixture is baked together, the more completely the reaction has occurred. The table contains some of the most important data of two of the hitherto most completely investigated systems of several carbonates and sulphates.

Even the reactions, the intensity of which is assigned as "small" in the table occur in one or a few seconds, until they are stopped by the impenetrable films of the reaction-product formed.

In the inverted mixtures, for instance, $CuO+CaSO_4$, no reactions occur. Accordingly there was also no "baking-together" in these mixtures not even after heating them to much higher temperatures than in the reaction-mixtures.

The table shows very obviously, that every oxide is characterised by a relatively very small interval of reaction-temperatures, i.e. e.g. BaO reacts with *all* sulphates in the same interval. (These temperatures are besides not very different from the temperatures, at which BaO reacts with carbonates. Later researches will show more clearly the influence of the anion on the temperatures in question.) These intervals are however for the special oxides very different and differ from each other about 80–100°C.

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[1] Z. anorg. Chem. 122, 181, (1922); 128, 1 (1923), both together with J. Heuberger.

There is accordingly no relation between the dissociation temperature (760 mm.) of a salt and its reaction temperature with one of the oxides in question. (Concerning an influence of the metal of a salt, cf. p. 1328.)

These facts can in bold outlines be explained as follows: We know, that many oxides and above all those of the alkaline metals and alkaline earths absorb anhydrous acid oxides, e.g. CO_2 with great intensity from the air. Our reactions show, that this tendency is so decided, that these oxides (BaO,-SrO,CaO . . .) are able to attract the atom-groups in question even from such solid compounds, where they exist or can be formed, e.g. CO_2 from carbonates, SO_3 from sulphates, P_2O_5 from phosphates, etc. But the temperature must of course be sufficiently raised, corresponding to a necessary degree of mobility of the reacting space-lattices (oxide and salt). In analogy with the fact, that for instance BaO absorbs SO_3 more intensely than SrO and SrO more intensely than CaO, the reaction temperature, with, for example, $CuSO_4$, must be lower for BaO than for SrO and lower for SrO than for CaO. We can imagine this process by looking upon the conditions in accordance with the following rough picture. With regard, for example, to SO_3, the affinity of BaO is stronger than that of SrO and so on. Accordingly SrO requires greater amplitudes in the SO_4-group of a sulphate than BaO, and CaO greater than SrO, in order to be able to break loose the attainable three O-atoms and one S-atom, i.e. the temperature at which BaO decomposes, for instance, a sulphate must be lower than the corresponding temperatures with SrO and CaO. The fact, that the reaction interval is only in a smaller degree for a special oxide and a special salt type dependent of the cation, and of the dissociation temperature (760 mm.) of the salt, includes the certain proof that the reactions have nothing to do with a gaseous phase.

Thanks to the investigation of Schaefer and Schubert,[1] we now know that the anions (SO_4, CO_3 . . .) of the salts are to be looked upon as systems, in which the oscillations in question occur without influence from the metallic component. Our experience is evidently in the best accordance with this result.

If this interpretation is true then, a transition of a salt, of course producing a radical displacement of the space-lattice and accordingly exposing the particles to powers of affinity, must bring about a change of the normal reaction temperatures of this type of salt. It is probable, that the reaction-temperatures and the transition points will nearly coincide for those oxides, which normally, i.e. with salts of the same type, react at temperatures above the transition points. Accordingly it was found that $AgNO_3$ with its transition point at 160°C reacts with BaO, SrO and CaO at 169, 172 and 170°C respectively. Ag_2SO_4 has a transition point at 412°C. Since this temperature is higher than the normal reaction temperature of a sulphate (cf. the table) with BaO, but lower than the corresponding temperatures with SrO and CaO this is in the very best accordance with our considerations, that BaO reacts normally at 342°C but SrO and CaO both at 422°C.

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[1] Ann. Physik (4) **1916**, 283.

According to these considerations, it would at first appear probable, that the reaction temperatures of an oxide with the different members of a salt type would coincide perfectly, not forming an interval as they in reality do. The occurrence of an interval can however be explained as follows: The recorded temperature is nothing but the temperature at which the reaction occurs with a sufficient rapidity for the corresponding reaction-heat to be observed on the heating-curve. If we keep for instance, to the system of BaO and $CuSO_4$, it is accordingly necessary that a certain minimum number of the SO_4-groups—dependent upon the reaction-heat—are decomposed by BaO per unit of time. But the rapidity with which this occurs, is undoubtedly quite individual for the different sulphates. A sulphate, the SO_4-groups of which permit a slower distribution of the fragments moving over to BaO, must accordingly react at a higher temperature, than a sulphate, in which the process in question occurs more rapidly. These conditions are after all probably closely related to those, occurring at the general thermal dissociation, which, as known, takes place with a rate typical for each member of a salt-type (cf. p. 0000,0000). This difference in rapidity is probably a function of the metallic component of the salts. For the reactions in question it is also the sulphates of the most positive metals, which react at the highest temperatures ($BaO+SrSO_4$:372°; $NaO+CaSO_4$:370°, $NaO+MgSO_4$:369°, but BaO+ for instance, $ZnSO_4$:341°C). It is accordingly possible that the different temperatures of the intervals show the influence of the positive ions of the salts.

System	Reaction-heat kg. cal.	Intensity	Temp. (C) of the beginning of the reaction.	Temp. (C) of the dissociation of:	The highest temp. (C) of the experim.
$BaO+SrCO_3=$ $BaCO_3+SrO$.	6,5.	very small	398° ±5.	$BaCO_3$ about 1360.°	410.°
$BaO+CaCO_3=$ $BaCO_3+CaO$.	42,0.	great	344° ±2.	$SrCO_3$ about 1141.°	360°.
$BaO+MgCO_3=$ $BaCO_3+MgO$.	35,9.	great	345° ±5.	$CaCO_3$ 916.°	380.°
$SrO+CaCO_3=$ $SrCO_3+CaO$.	35,5.	great	464° ±4.	$MgCO_3$ about 546°.	480°.
$SrO+MgCO_3=$ $SrCO_3+MgO$.	29,4.	small	456° ±4.	$BaSO_4$. 1300°.	470°.
$CaO+MgCO_3=$ $CaCO_3+MgO$	9,3.	very small	523° ±1.	$SrSO_4$. >1130°.	535°.
$BaO+SrSO_4=$ $BaSO_4+SrO$.	11,4.	small	372° ±2.	$CaSO_4$ >1060°.	490°.

$BaO+CaSO_4=$ $BaSO_4+CaO$.	46,0.	great	370° ±6.	$MgSO_4$ $>940°$.	450°.
$BaO+MgSO_4=$ $BaSO_4+MgO$.	54,8.	very great	369° ±1.	$ZnSO_4$ $>830°$.	440°.
$BaO+ZnSO_4=$ $BaSO_4+ZnO$.	69,7.	very great	341° ±5.	$CoSO_4$ $>740°$.	440°.
$BaSO+CoSO_4=$ $BaSO_4+CoO$.	56,3.	very great	328° ±14.	$CuSO_4$ $>660°$.	440°.
$BaO+CuSO_4=$ $BaSO_4+CuO$.	68,4.	very great	346° ±0.		480°.
$SrO+CaSO_4=$ $SrSO_4+CaO$.	34,7.	small	451° ±5.		540°.
$SrO+MgSO_4=$ $SrSO_4=MgO$.	43,5.	great	441° ±3.		550°.
$SrO+ZnSO_4=$ $SrSO_4+ZnO$.	58,3.	great	424° ±3.		490°.
$SrO+CoSO_4=$ $SrSO_4+CoO$.	45,0.	great	431° ±1.		510°.
$SrO+CuSO_4=$ $SrSO_4+CuO$.	57,0.	great	418° ±7.		460°.
$CaO+MgSO_4=$ $CaSO_4+MgO$.	8,8.	very small	about 540°.		640°.
$CaO+ZnSO_4=$ $CaSO_4+ZnO$.	23,6.	small	520° ±6.		650°.
$CaO+CoSO_4=$ $CaSO_4+CoO$.	10,3.	very small	533° ±4.		670°.
$CaO+CuSO_4=$ $CaSO_4+CuO$.	22,4.	small	516° ±5.		640°.

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December, 1928.

NEW BOOKS

Physikalische Chemie der Zelle und der Gewebe. *By Rudolf Höber. Part II, Fifth edition. 25 × 17 cm; pp. xvi + 360. Leipzig: Wilhelm Engelmann, 1924. Price, paper: 12 gold marks.* The first part of this volume was reviewed about a year ago (27, 692). The second part is a treasure-house of unexplained facts. The chapters are entitled: distribution and adsorption with pharmacological phenomena; the physiological action of electrolytes on cells and tissues; electrical processes at physiological surfaces; resorption, formation of lymph, and secretion; the physical chemistry of metabolism.

In general, there is a parallelism between the effectiveness of a narcotic and its distribution ratio for oil and water. Anaesthesia occurs when the concentration of the narcotic in the lipoid is about 0.06 mol, p. 552. The combustion of charcoal and the decomposition of hydrogen peroxide by platinum may be poisoned in the same way as the combustion in the cell, p. 557. Alcoholic chloroform decreases the permeability to water of certain membranes from the frog; when more chloroform is used, the transfer of water is decreased still more, but the permeability of the membrane to sodium chloride is increased, p. 574. On p. 576 the author raises the question as to what physical chemical changes in the surface of protoplasm account for the changes in permeability produced by narcotics. He draws the obvious conclusion that poisoning and adsorption must run appromixately parallel, p. 581, and then adopts the view, first put forward by Michaelis and Takahashi, that haemolysis outside of the neutral region is due to the coagulation of the cell colloids, p. 598.

The isoelectric point of blood is displaced toward the acid side by sodium chloride, p. 604. "We have seen that, according to Michaelis and Rona, the isoelectric point of colloids is also displaced by salts; the anions displace it toward the acid side and the cations toward the alkaline side, the effect being more marked the more strongly the ions are adsorbed." "The adsorption of ions and especially of albuminoid ions is an essential factor in determining the surface potential difference for blood corpuscles, p. 612.

"The action of salts on plant cells is comparable with their action on the red blood corpuscles. We have already seen that plant cells are so damaged by pure salt solutions that their permeability becomes abnormal. From the experiments of Osterhout, Fitting, Tröndle, Kahho, and others, it appears that the permeability increases in solutions of salts of the alkalies, finally developing into cytolysis. With cells containing a colored juice, the exosmosis can be seen easily. In solutions of salts of the alkaline earths and also in solutions of salts of other bivalent cations (Co, Mn, Fe, Ni, Zn, Cd, Sn) and of trivalent and quadrivalent cations (Ce, V, La, Th), the permeability decreases, at least at first, though afterwards increasing irreversibly", p. 619.

While acids are generally toxic to water animals and while the effect is due chiefly to the concentration of hydrogen ion, a comparison of inorganic and organic acids shows that there are other factors; for the organic acids are much more toxic to certain infusoria than the hydrogen ion concentration justifies, p. 628. If we place frog's muscles in solutions of sodium salts equivalent to 0.2% NaCl and make the solutions presumably isotonic with the frog by addition of cane sugar, it is found that there is a marked effect due to the anion, p. 630. Höber considers that the changes in permeability are due chiefly to peptization or coagulation of the colloids either at the surface of, or inside, the cell, p. 650.

From experiments on deplasmolysis, Netter concludes that the antagonistic action of bivalent and univalent cations is about neutralized when the ratios of sodium to the other cations are: Ca, 75; Sr, 40–50; Ba, 5-10; Co and Ni, 50; Mn, 5; and $Co(NH_3)_6$, 40, p. 662. In some cases, as with certain sea algae, we are dealing primarily with the swelling of the membrane, p. 668. In one case of this sort the neutral ratio of sodium to calcium was 250. With *Fundulus* there is a mutual antagonism between sodium and potassium ions, p. 670. The relative effects of sodium or potassium ion and calcium ion on the heart-beat may reverse if the point of application is changed, potassium ion increasing the rate under one set of conditions and decreasing it under another set, p. 688.

When studying physiological potential differences, Höber distinguishes between "oil" cells and "membrane" cells. In the first we have a second liquid phase due to lipoids and in the second we have some form of the Donnan equilibrium, pp. 694-705. From the effect of dyes on the potential differences, Höber concludes that the more important electrical currents in animals and plants are not due to "oil" cells, p. 709. From the view-point of the "membrane" cells, a stimulated nerve behaves "as though the plasma film were perforated, the hole closing again as soon as the stimulation has ceased," p. 715. There is a drawing on p. 716 showing how the electric eel might work: but nobody ever discusses the question of insulation, though that seems an important matter to the electrochemist if one is dealing with potential differences of five hundred volts.

If a dilute grape sugar solution is placed in the intestine of a dog, water is taken out more rapidly than sugar, so that the sugar concentration increases; but practically no sodium chloride passes in the opposite direction. If the same solution is placed in the stomach of a rabbit, the concentration of sugar drops and a good deal of sodium chloride moves in the opposite direction, p. 756.

The skin of a frog is apparently permeable to water and consequently the frog takes up water continually from fresh water, p. 772. Continuous urination is therefore the only thing that saves him from bursting and that is how he survives. This seems to involve one membrane through which water passes into a solution and another membrane through which water passes out. If this took place automatically, each frog would be a miniature power plant. The only other explanation seems to be that he is a continually-acting pumping-station and, at that, he must have some very interesting valves somewhere. Höber admits, quite frankly that our knowledge in regard to the theory of secretions is still practically nothing, p. 792. "Filtration, resorption, and secretion are catch-words which have appeared prominently for decades as explanations for the elimination of urine." Caffeine apparently owes its diuretic action to the fact that it increases the dispersity of the serum and therefore the rate of filtration, p. 803.

When a tired muscle recovers in presence of oxygen, the consumption of the latter is only enough to account for one quarter of the lactic acid that disappears, while the amount of carbon dioxide formed corresponds to the oxygen consumed. Three-quarters of the lactic acid must therefore be converted into some other substance and this proves to be grape sugar or glycogen, the reactions being.

$$8\ C_3H_6O_3 + 6\ CO_2 + 6\ H_2O + 3\ C_6H_{12}O_6$$

$$3\ C_6H_{12}O_6 = \frac{3}{n}\,(C_6H_{10}O_5)_n + 3\ H_2O.$$

Many organisms cannot live in oxygen at pressures of 10-12 atmospheres; but they do not die, as one might assume, from too rapid oxidation. They behave as though there were a lack of oxygen, p. 874. Höber cites the cases of phosphorus not glowing in pure oxygen as analogous; but it is something of a question whether this point is well taken.

These few citations will give a fair idea of the calibre of the book. Nearly every page suggests an article that one would like to write if one only knew enough.

Wilder D. Bancroft

World Weather. *By Henry Helm Clayton. 23 × 16 cm. pp. xx + 393. New York: The Macmillan Company, 1923. Price: $4.00.* In the introduction the author says: "The weather in some form or other affects every living creature. It has been the topic of universal conversation. It is the subject naturally mentioned in beginning a chat with a friend or stranger. It has been the foundation of endless jests and it has furnished a theme for countless poems. The sparkling air, the brilliant sunshine, the drifting feathery snow flakes, the pattering rain have brought joy to millions and yet the angel of death rides in the trail of the icy blast. The same wind may bring to one the intensest joy and to another the deepest tragedy. The same rain which brings tears to the eyes of a maiden robbed of an expected outing may bring smiles to an agriculturist, who sees in it the promise of an abundant crop. The same snowstorm may bring joyous anticipation of sport to a youth and may bring death to an aged neighbor. The stakes depending on the changes of the weather are so vast, that those dependent on the turns of the wheel of chance at Monte Carlo seem as nothing in the balance. But a risk dependent on the weather is not a gamble. The gambler stakes his all from choice in pursuit of excitement or gain, while the man whose welfare depends on the turn of the weather is bound by thongs of necessity. As mankind must be fed, the farmer must sow his seed and watch the turn of the weather which brings him abundance or want. The manufacturer must send his goods from regions where power is procured easily to other regions more favorable for food production, and risk their loss by the destructive hurricane. The merchant must bring his products from places where they are most readily grown to those where they are most needed, and risk their loss by moisture, heat or cold. In the United States alone more than ten thousand million dollars are taken from the soil each year. Fortunately, nature never completely deprives the grower of needed moisture, but the total difference in value between the amount grown in a year of abundant rain and a year of deficient rain may easily be five hundred millon dollars.

"The toll of sickness and premature death and of losses to business from a lack of adjustment to unexpected changes of weather is so vast that it staggers all computation. It is not strange that the subject of the weather has occupied so much of the thoughts of mankind, and in the following pages an attempt will be made to explain a part of the vast stock of knowledge accumulating about the weather, especially those newer researches which indicate that the time is near at hand when weather changes can be anticipated so far in advance, as to save much of the loss and distress which now follows in the wake of the unexpected adverse conditions.

"The work of the meteorologist has a spiritual as well as a material value. In no other way has man been more haunted by degrading superstitions than in his interpretation of the signs of the sky and air. The shining crosses formed by the sunlight in the filmy cirrus clouds, the blood-red rain, the fiery sunsets, the reverberating thunder, the blinding flashes of lightning, the pulsating aurora filled him with untold terrors; his terrible losses from prolonged droughts led him to load the air with sound by the beating of tom toms and even at times to sacrifice human victims to appease the anger of the Rain God. Through scientific research, these things have now found their natural explanation and man has learned that the universe is governed by well-regulated laws and not by angry impulse. Religion is slowly becoming elevated to the higher plane of spiritual intercourse, and is freed from the meaningless rites to appease an angry God."

The headings of the chapters are: the forces controlling weather changes; the daily period in the weather; the yearly period in the weather; temperature and the weather; pressure and the weather; wind and the weather; moisture, clouds, and rainfall; cyclones and anticyclones, or storms and sunshine; sky colors and visible signs of the sky and air; and the sun and the weather; physics of the air in relation to solar and terrestial radiation; periodicity in the weather and in solar phenomena; forecasting the weather; meteorology of the sun.

"The isolated cumulus and the isolated cirrus are really clouds of the same nature caused by local ascending convection currents, but at different levels and at different temperatures. When cumulus are formed at a very low temperature there are frequently seen long fibers streaming behind, due to falling snowflakes, and the upper part evaporates slowly and is drawn out into cirruslike bands. Ordinarily the light particles of rain falling from the base of the cumulus are quickly evaporated, but in arid regions streaks of rain which do not reach the earth's surface are seen falling from large cumulus clouds forming cirruslike fibers, but of a dark color. That the long fibers which stream downward and backward from tufts of cirrus are really snow-flakes has been proved by Berson and other aëronauts who have intercepted them when ascending to great heights. The slow evaporation of the cirrus also permits it to be drawn out into long bands, by wind currents of different velocities; while the top of the cumulus, when carried beyond the local ascending current quickly evaporates. The slow evaporation of the cirrus is due to the extremely low temperature in which it is formed, some sixty to seventy degrees below zero Fahrenheit (about −65°C.)."

Along with this one should include the paragraph written by Aitken in 1891. "We see from the observations made with the fog-counter, that, whenever a cloud is formed it at once begins to rain, and the drops, though small in size, shower down in immense numbers. These drops fall into the air under the cloud, where they evaporate if the air is dry, and the distance they fall will depend on their size and the dryness of the air underneath. So that on a summer day with white clouds passing overhead, it is really raining; but the drops, being very small, evaporate in the air under the cloud long before they reach the earth. It seems probable, therefore, that much of the melting of clouds is produced in this way the particles falling from the saturated air in which they were formed and dissolving in the drier air underneath."

On p. 172 there are some very interesting facts in regard to thunderstorms by aviators who have been in them. "Lieutenant Cobb was stunting near Love Field, Texas, at about 3500 feet altitude during the approach of a thunderstorm. After doing three evolutions, taking about fifteen minutes he found that he had gained some 3500 feet (1100 m.) in altitude, instead of losing 1500 feet (500 m.) as was usual. Sometimes the lifting would be of the order of 500 feet in a minute.

"This indicates that there was a wind with an average vertical component upward at about 5 miles per hour (2m. per second) blowing toward the storm. At the end, the aviator noticed sharp mammato-cumulus above. and strato-cumulus clouds below him. He seemed to be at an altitude about midway between them, though he was some 5 miles (8 km.) away from the storm front. On decending, he entered extremely bumpy air and was able to land only by driving into the wind with the engine on.....On another occasion Lieutenant Morgan, while flying in front of a thunderstorm, was suddenly lifted from 2000 to 7000 feet (700 to 2300 m.).

"The American aeronaut Wise once made an ascent in front of a thunderstorm and was drawn by an ascending current into the thunder cloud. When in a cloud, he was caught in a whirl and spun around in a circle with frightful rapidity. The air was intensely cold, so that his beard, his clothes and the rigging of the balloon were soon encased in ice. He was pelted by driving rain, mingled with hail and snow, and in the meantime his balloon was drawn steadily upward to the top of the cloud, where it was thrown outward into the clear air. At a short distance from the cloud it began to descend rapidly and he expected soon to be safe on the firm earth after his thrilling experience; but when near the base of the cloud he was drawn into the cloud and again passed through the terrible maelstrom to the top of the cloud, but now, with all his ballast and most of his gas gone, he came down with such rapidity that he passed through the indrawing stream of air and reached the ground in safety, his balloon-cover acting as a parachute.

"This experience of Wise suggests the method of hail formation. The drops of water carried to the top of the cloud by the swift ascending current are frozen by the intense cold, and, passing out of the ascending current at the top of the cloud, fall to the base of the cloud, where they are once more drawn into the whirl, there covered with water and ice and carried to the top of the cloud from whence it again falls. This process may be repeated until the hailstone is too heavy to be lifted by the ascending current, when it would fall to the ground. In this way the various concentric coats of the hailstone are explained. When the whirl in the thunderstorm becomes exceptionally strong it extends downward below the base of the cloud, develops a funnel and becomes the fearful tornado or waterspout."

In the chapter on forecasting the weather, p. 325, Clayton says that "sky colors have also been immemorially an aid to short-range weather forecasting. From the earliest historic times there are quotations showing that sunset and sunrise colors have formed a basis for weather forecasts for the same day or the succeeding day. In English these signs have embodied themselves in such rhymes as

Evening gray and morning red
'Twill pour down rain on traveler's head;
But evening red and morning gray
Will set a traveler on his way.

"All such forecasts are based on the fact that storms move in general from west to east, and dense banks of condensed vapor towards the west cut off the colors and light of the sun, so that when it sets in a gray mass the approach of conditions favorable for rain is indicated. On the other hand, when the gray is found in the east at sunrise, the storm has already past or is passing. A rosy sunset indicates fair weather toward the west, from which direction the weather to be expected comes.

"Unusual transparency of the air and pure twilight colors indicate cooler, fair weather for the next day, although frequently followed within two days by additional rain; while hazy air, in which the sun sets as a fiery ball, attends droughty conditions with temperature above the normal of the season."

Clayton does not cite the interesting observation by Aitken that the visibility of the phenomenon known as the "Old Moon in the New Moon's Arms" must depend on the illumination by earth light of the part of the moon which is in darkness as regards the direct solar rays. The phenomenon will therefore be best seen when the regions to the west are covered with vast areas of cloud from whose upper surface the sunlight is strongly reflected. There is thus a great probability that the "Old Moon" when distinctly seen is a herald of wet weather.

Wilder D. Bancroft

The Theory and Application of Colloidal Behavior. *By R. H. Bogue. Vols. I and II. 21 × 15 cm; pp. xxvi+444; xxvii+386. New York and London: McGraw-Hill Book Co., 1924. Price: $.800 per set.* The first volume deals with the theory of colloidal behavior, the subheads being: heterogeneous equilibria; surface kinetics; adsorption and catalysis; structure. Under heterogeneous equilibria the single chapters are: application of the thermodynamics of heterogeneous equilibria to the theory of colloidal behavior, by John Arthur Wilson; crystalloidal behavior of proteins, by Jacques Loeb; the flocculation and stability of colloidal suspensions by John H. Northrop; the colloidal behavior of the body fluids, by Donald D. Van Slyke.

There are four chapters under surface kinetics: the kinetics of disperse systems, by E. Franklin Burton; surface energy in colloid systems by William D. Harkins; the theory of emulsification, by Joel H. Hildebrand; and emulsions and foams, by Harry N. Holmes. The section on adsorption and catalysis contains six chapters: adsorption in colloid systems, by Leonor Michaelis; adsorption and catalysis, by Wilder D. Bancroft; colloid chemistry and contact catalysis, by Hugh S. Taylor; sensitization by means of hydrophile coollids, by Herbert Freundlich; mutual reactions of colloids, by Arthur W. Thomas: enzymes, by E. Frankland Armstrong.

Under structure there are only three chapters: jellies and gelatinous precipitates, by Harry B. Weiser; the study of soap solutions and its bearing upon colloid chemistry, by James W. McBain; viscous and plastic flow in colloid systems, by Eugene C. Bingham.

The second volume is devoted to the application of colloidal behavior, and the general sub-heads are mineral products, vegetable products, and animal products. The seventeen chapters are: the colloid chemistry of minerals and ore deposits, by Waldemar Lindgren; the colloid chemistry of the soil, by Milton Whitney, colloidal phenomena in metals and alloys, by H. W. Gillett: coal, coke and tar, by A. C. Fieldner, Reinhardt Thiessen and J. D. Davis; colloids and fuel, by S. E. Sheppard; the precipitation of smoke and other suspensoids in gases, by William W. Strong; the colloid chemistry of silica and its derivatives, by William Stericker: the colloid chemistry of the cereals, by Carl L. Alsberg; fruit jellies, by Lester W. Tarr; cellulose and its derivatives, by Gustavus H. Esselen, Jr.; rubber, by G. Stafford Whitby; the significance of colloids in the dietary, by E. V. McCollum; leather, by Henry R. Procter; gelatin and glue, by Robert H. Bogue; colloid chemistry and the photographic process, by S. E. Sheppard; casein and the dairy industry, by Harper F. Zoller; sanitation, by John Arthur Wilson.

The editor has got together a rather remarkable group of papers, most of them by people who know their subject well. He is much to be congratulated on the result. In the preface the editor makes it quite clear that he belongs to the Loeb school; and the articles by Wilson, Loeb, Thomas, Procter, and Bogue are a further confirmation of this statement. While some of the permanent value of the book has probably been sacrificed to this viewpoint, the volumes are more interesting reading and will appeal to a larger circle. The editor is therefore justified on the grounds of expediency.

The two volumes are a welcome addition to the literature of colloid chemistry, and justify the statement of the editor in the preface that "this plan has evolved a work that has a direct and purposeful objective, and it will prove the more useful to the greater number of students of colloidal behavior. Every large college and university is now offering some work, at least to graduate students, in colloid chemistry. Many books are available for an elementary presentation; but no attempt has heretofore been made to gather together material for an advanced text or reference work, nor to present the actual application of the science. The editor believes that these ends are achieved by the publication of this book. It is written for the student and the investigator, the research man and the practical man, who, in science or in industry, is concerned with the problems of colloidal behavior."

Wilder D. Bancroft

Licht und Farbe in Kolloiden. *By Wolfgang Ostwald. Part I. 24+17 cm; pp. xiv+556. Dresden and Leipzig: Theodor Steinkopff, 1924. Price: $8.30.* This is a pathetic book. The manuscript was practically completed in 1914; but of course could not be published then. During the war the author could not work on it and conditions in Germany have been such since the war that no revision has been possible. Consequently this is a book which is practically ten years out of date on the day that it is published. Just to cite a few instances, the author does not know about Holmes' chromatic emulsions, Martin's work on the scattering light by pure liquids, or Mason's work on the colors of feathers. As regards the peacock Ostwald is a strong upholder of Walter's view that it is a case of selective reflection by solid pigments. This was perfectly proper in 1914; but it is hopelessly wrong in 1924. A very elaborate chapter on the ultra-microscope is hardly as valuable now as it would have been in 1914. The book would have been an admirable one in 1914; but now its value is chiefly as a mass of collected material, the view of the author not being especially helpful.

Ostwald gives a good many pages to the subject of 'metallic' colors; but, as is so often the case with him, it is difficult to find out what he really believes. The nearest that he comes to it is, p. 374, that they are due to anomalous dispersion, abnormal reflection, and abnormal absorption; but he cannot mean that because the metallic colors of birds and butterflies are almost entirely the colors of thin films and thin films do not show anomalous dispersion or abnormal absorption.

The first three chapters deal with optical heterogeneity of colloid systems, the Tyndall beam and the ultramicroscope. The fourth chapter deals with polarization in colloid systems and the fifth with the rotation of the plane of polarized light by colloid systems. The sixth chapter is devoted to absorption by colloids, with "refraction colors, diffraction colors, and colors due to selective reflection" as a sub-title. Interference colors are mentioned in the text, p. 364; but are dismissed in about two pages with mother-of-pearl as the chief illustration. The subject of the seventh (and last) chapter is refraction and double refraction in colloids.

One very interesting statement is the conclusion by Drude, p. 71, that the index of refraction of silver increases from 0.18 to 4.0 as the thickness of the film decreases from 10.3 $\mu\mu$ to 1.5 $\mu\mu$. Another interesting one is, p. 344, that sodium dissolved in liquid ammonia has more coloring power than aniline blue in water. A third one is, p. 371, that chromic oxide peptized by chromic salts is a liquid analogue of the gem Alexandrite, being green by daylight and red by candle light. A fourth is, p. 67, that the refractive indices of cobalt for yellow light and of selenium for green light far exceed the corresponding values for the diamond.

Wilder D. Bancroft

Elementary Physical Chemistry. *By W. H. Barrett. 18+14 cm; pp. viii+247. London: Edward Arnold and Co., 1923. Price: $1.80.* In the preface the author says that "a course of elementary Chemistry or Physics is usually, at the present day, made fully experimental; but in approaching Physical Chemistry the beginner very often sees and performs few or no illustrative experiments, and consequently often views that subject in false perspective." This may be true in England but it is certainly not true in general in the United States. Another statement on the same page is that "many beginners regard Physical Chemistry as a collection of disconnected subjects, and therefore in this book an effort has been made to preserve continuity by making the kinetic-molecular hypothesis the basis of the whole treatment." The reviewer had supposed that this particular fault was one from which physical chemistry was exceptionally free and he is quite certain that the remedy is more deadly than the thing it is to cure.

We may talk about molecules and most of us do; we may believe in molecules and some of us do; but it is extremely doubtful whether any chemist ever really had a convincing mental picture of a solid as a mass of vibrating molecules. It can't be done and consequently it is extremely doubtful whether it is wise to stress this side when teaching a beginner. Why not use language that means something to the hearer?

While the reviewer believes that the first chapters are too difficult, he also objects to the following passage, p. 179, because it tries to be too simple. "Ostwald's theory of the colour change of an indicator is that the ions of the indicator possess one colour and the undissociated indicator a different colour. Modern theory regards the colour change of an indicator as a more complicated process involving a tautomeric change in addition to an ionic change; but fortunately the deductions from Ostwald's simpler theory for our purpose are identical with those from the more complex theory, so we will here adopt the simpler theory." The student is quite able to grasp the idea of a secondary, reversible change in the undissociated base or acid which gives rise to a color change. There are some advantages in not telling a student a thing which he knows is not so. Incidentally, the reviewer objects to the next statement, p. 179, that "most common indicators are weak acids." Methyl orange is a weak base so far as its indicator properties are concerned.

It is only fair to state that the author's bark is worse than his bite. The kinetic-molecular theory is more prominent in the preface and in the running heads than in the text. Whenever the author forgets his high moral mission, he does very well indeed and the experiments seem to be fairly well chosen. Whether one wants a combined text-book and laboratory manual is a matter of temperament and training. Apparently this particular type is thought well of in England.

Wilder D. Bancroft

The Chemical Elements. *By F. H. Loring. 22+15 cm; pp. viii+171. New York: E. P. Dutton and Company, 1923. Price: $3.75.* "The aim of this book is to present in a simple and concise form certain characteristics of chemical elements as studied from the point of view of their quantitative grouping and their structural binding—using the latter term in a wide sense—and to bring into prominence the significance of 'space physics' as applied to certain phenomena involved," p. v.

Each chapter is summarized, which is not a bad idea, though it is not especially helpful with such short chapters. "The absence of certain elements in the seventh places of the periodic table; the small quantities of scandium in existence relative to the elements on either side of it, the missing of places I and VII in radio-active changes; the number of existing rare-earth elements Pr to Lu inclusive being by certain considerations limited to 13, and being in harmony with a blank atomic-number lacuna 54+7; are all accounted for by one or two types of mathematical series based upon atomic-number differences, the series also having a limiting characteristic in agreement with the extent of the atomic numbers. The deduction therefrom follows that these missing elements do not exist, or if they do exist are present in exceedingly minute quantities," p. 29.

"The relative distribution of elements in the earth's crust, according to the findings of Clarke and Washington, is tabulated and shown to support the view that scandium exists in relatively small quantities compared with the quantities of calcium and titanium situated on each side of it in the periodic table, and this fact strengthens the conception of a significant atomic number series, thereby earmarking the periodic places where no elements can fall, or if they do fall into such places the quantities will be exceedingly minute," p. 35.

"The existence of scandium in the sun does not necessarily invalidate any relative quantitative deduction as to the proportionate amount of this element relative to those on each side of it in the atomic-number series; for the sun may be manufacturing or degrading practically all of the existing elements, and any excess of one in particular may not appear in large relative quantities in the final state when this process of manufacture and (or) degradation is finished," p. 44.

Wilder D. Bancroft

Problems in General Physics for College Courses. *By Morton Masius. Second revised and enlarged edition. 21+14 cm; pp. x+164. Philadelphia: P. Blakiston's Son and Co., 1924. Price: $2.00.* The first edition was reviewed in 1918 (**22**, 458). The second edition contains nearly four times as many problems. The reviewer is glad to endorse the sentiments on p. 4. "It is manifestly impossible to memorize ready-made formulae for all possible cases. Hence the general plan of memorizing only the most important relations, and making the necessary deductions from them according to the problem under discussion. All students will admit the force of the argument just given, but another question may now arise. If, in general, it is a safer plan to rely not on a large number of memorized formulae, but on the power of being able to deduce the special formula required for a particular problem, is any memory work required at all? Would it not be better to leave everything to reasoning power and not memorize any formulae? The answer to these questions is: No. The reason for this is very simple. In the list of the equations that are to be memorized we have included two kinds: (1) those that express the fundamental laws, (2) those that occur very often. The reason for memorizing those of the second class is obvious. As regards those of the first class we must recall that no amount of logical reasoning, however original and profound, can produce a *definition* or a *fact*. A knowledge of a few definitions and facts is necessary, and all relations representing them have to be memorized."

Wilder D. Bancroft

ERRATA

In the paper by Messrs. Bhatnagar and Shrivastava the heading of column 6 in Tables II-VII, pp. 733-738 should be changed from "Quantity of sucrose [glucose, galactose] adsorbed per 100 cc of the mixed solution examined" to "Quantity of sucrose [glucose, galactose] adsorbed per 100 cc of the sugar solution"; and the headings of Column 7 in the same tables should be changed from "Quantity adsorbed per 100 cc of the sol" to "Quantity adsorbed by the mixture containing 100 cc of the sugar solution and the sol in the corresponding ratio indicated in Column 2.

In the paper by Mr. Perry, p. 108, the equation of state for helium should read:

$$P = \frac{20.53T}{V-3.17} - \frac{3285}{(V+6.85)^2}$$

In the article as published, the T was omitted.

On pp. 893 and 896 the titles and authors have been transposed. The proper heading for the book review on p. 893 is **Lehrbuch der Metallographie.** *By Gustav Tammann.* The proper heading for the book review on p. 896 is **Metallographie in Elementarer Darstellung.** *By Rudolf Ruer.*

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