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[Mechanism of the Acetacetic Ester Synthesis. I.]

THE CONDENSATION OF ACETONE WITH OXALIC ESTER

BY ROBT. H. CLARK

Acetacetic ester was first prepared by Geuther,[1] in 1863, by the action of metallic sodium on ethyl acetate. It has since become one of the most important agents in organic synthesis; even in 1898 the bibliography of the ester and its derivatives, published by the Smithsonian Institution, occupied 148 pages.

Twenty-five years after Geuther's discovery, W. Wislicenus and L. Claisen showed that a large class of substances, chemically analogous to acetacetic ester, could be prepared by the action of metallic sodium or of sodium ethylate on esters, mixtures of esters, or mixtures of esters with ketones. They thus, in a sense, generalized Geuther's reaction; and their work has proved of the very greatest importance to chemistry, both pure and applied.

These discoveries led Claisen to a new theory of the formation of acetacetic ester; or, to be more accurate, it was the desire to put his new theory to the test that led to his experimental discoveries.

Kolbe,[2] and after him v. Baeyer,[3] explained the formation of acetacetic ester from ethyl acetate by assuming the primary formation of a sodium- or disodium-acetic ester, $CH_2Na.COOEt$, or $CHNa_2.COOEt$; and this theory in Baeyer's hands led to the synthesis of phloroglucin from sodium malonic ester, a most important step in his classical work on the constitution of benzene.

Claisen[4] rejected this view, and suggested in its place that Geuther's reaction is due not to the direct action of

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[1] Göttinger Anzeigen, 1863, 281.
[2] Zeit. f. Chem., 10, 637 (1867).
[3] Ber. chem. Ges. Berlin, 18, 3460 (1885).
[4] Ibid., 20, 651 (1887).

sodium, but to that of sodium ethylate, which forms an addition product with the ethyl acetate; and that this reacts with more of the ethyl acetate to form acetacetic ester, thus:

$$CH_3.COOEt + EtONa = CH_3.C(ONa)(OEt)_2.$$
$$CH_3.C(ONa)(OEt)_2 + CH_3.COOEt = CH_3.C(ONa):CH.COOEt + 2EtOH.$$

This theory of Claisen's has been generally accepted, but ever since its first appearance it has been attacked by Michael; the controversy between these two chemists on this subject has not even now come to a conclusion, and an important review of the argument by the latter has recently been published.[1]

Michael's principal argument against Claisen's views is based on the fact that while metallic sodium acts readily on ethyl acetate and gives a good yield of acetacetic ester, sodium ethylate acts only at high temperatures, and gives a poor yield. The fact that "absolute" ethyl acetate, from which the last traces of alcohol (that could serve to make sodium ethylate) have been removed, will not act with sodium at all, he classes with the numerous reactions that will not take place unless in presence of a trace of water—that between sulphuric acid and metals, for instance. And Claisen's "experimentum crucis," *viz.*, that isobutyric ester forms no condensation product analogous to acetacetic ester, he explains on grounds of his own.

Claisen, in reply, deals at length with the action of metallic sodium on ethyl acetate, pointing out that if merely a trace of alcohol be present the reaction begins slowly, and that the rate increases as the reaction proceeds and more alcohol is formed, according to the equation quoted above. This alcohol reacts with the sodium and produces the necessary ethylate. The unsatisfactory yield, when sodium ethylate itself is substituted for metallic sodium, he explains by stating that the reaction between sodium ethylate and ethyl acetate is reversible, and that the product is de-

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[1] Ber. chem. Ges. Berlin, 38, 709 (1905).

composed by alcohol; if sodium is present, the alcohol formed by the reaction is at once decomposed, otherwise it accumulates and spoils the yield.

In defending his theory, Claisen thus perhaps unconsciously appeals to the principles of chemical kinetics and equilibrium; but his main argument is based on the analogy between the acetacetic ester synthesis and the condensations discovered by himself and Wislicenus. One explanation must do for all, he says; and that must be the ethylate explanation, for many of these condensations may be carried out successfully in dilute alcoholic solutions of that substance.

The methods of physical chemistry for attacking problems such as this, which deal with the mechanism of reactions, have all grown up since Claisen's first paper was published, and have not hitherto been applied to the elucidation of this particular question. It seemed, therefore, desirable to test the validity of Claisen's assumption that the condensation of esters with esters is identical with that of ketones with esters; and to see whether the results of kinetic measurements can be brought into line with his theory of the synthesis.

The reaction between ethyl oxalate and ethyl acetate was selected as typical of one group, and that between ethyl oxalate and acetone of the other. The present paper contains the results of my measurements on the rate of the latter, while Mr. H. C. Cooke is engaged with a study of the former reaction; the condensation of acetophenone with acetic ester is also being studied in this laboratory. It is proposed to publish the results of these investigations as they are obtained, and to postpone theoretical discussion until the material has been collected.

In investigations of this kind it is necessary to be provided with some means of stopping the reaction at will, and of determining the amount of change that has taken place. In the present case, the first end was attained by neutralizing the sodium ethylate, and the second by determining the depth of color produced by the addition of a solution of ferric chloride.

The feasibility of this method of analysis was ascertained only after a number of experiments with pure acetonoxalic ester and ferric chloride, and the unexpected nature of some of the facts disclosed during these experiments led to an extension of the study of this ferric reaction beyond the limits necessary for the foundation of an analytical method.

An account of my experiments on the ferric chloride reaction follows the description of the method employed in preparing the acetonoxalic ester, and is followed in turn by the measurements of the rate at which the latter substance is synthesized.

Preparation of Acetonoxalic Ester

The method of preparing this substance as given by Claisen[1] consists in adding a mixture of one mol each of acetone and oxalic ester to an alcoholic solution of one mol of sodium, boiling off the alcohol, and fractionating the ester in vacuo.

In my first attempts to follow these directions I got absolutely no yield, and even when the experiments were repeated with Merck's best acetone, Kahlbaum's absolute alcohol, and Kahlbaum's ethyl oxalate, the result was not much better. In the end, I found that the trouble was caused by the presence of traces of water in the "absolute" alcohol employed, and it was only when I discarded Kahlbaum's and Merck's preparations and worked with Squibb's that satisfactory results were obtained. This extreme sensitiveness of the reaction to water is not hinted at anywhere in the literature.

In the presence of a trace of water, sodium ethylate and oxalic ester in alcoholic solution give a whitish gelatinous precipitate, which is quickly formed and is quite distinct in appearance from the yellow denser precipitate of sodiume acetonoxalic ester. In my experiments I was even unable to empty the pipettes by blowing through them, for fear of the deleterious action of the water so introduced into the

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[1] Ber. chem. Ges. Berlin, 20, 2189 (1887).

reacting mixture. A few quantitative measurements showing the effect of traces of water on the yield of acetonoxalic ester are given on page 11.

Instead of fractionating the ester, which I found to be accompanied by losses, I purified it by freezing; the following is a full description of my method of preparation: 58 grammes of acetone and 146 grammes of ethyl oxalate were mixed in a liter flask, and cooled in ice water; a solution of 23 grammes of sodium in 460 grammes of absolute alcohol was then slowly added. In the course of an hour the sodium compound had separated completely; it was freed from the mother-liquor by filtration through cheesecloth, and pressed between filter paper. The sodium compound was then weighed, and slightly less 30 percent sulphuric acid added than enough to neutralize the sodium present. An oil separates, which is dried in a vacuum over calcium chloride, and the acetonoxalic ester separated from it in the form of crystals by freezing in a bath of ice and salt. So prepared, the ester melts at 18°, and boils at 210° (thermometer in vapour) at a pressure of 753 mm.

Acetonoxalic Ester and Ferric Chloride

A series of preliminary experiments showed that the deep red colour produced by ferric chloride in solutions of acetonoxalic ester was not affected (when viewed longitudinally, through a column of liquid in a test-tube) by addition of water, alcohol, acetone or ethyl oxalate if the ferric chloride is in large excess, but that the colour grew fainter if sodium ethylate, or any alkali or acid was added; alkalies seemed to have more effect than acids. On warming, the tint grew darker, the original colour being restored on cooling, but a difference of ten degrees had little effect on the colour.

Colorimeter

A colorimeter was then set up, consisting of two small test-tubes of the same size and form, with flattened bottoms; one of them was provided with a side tube sealed on near the bottom, and served for the standard solution, the other took the sample to be analyzed. Attached by rubber to the side tube was a glass tube of one centimeter bore, which could be moved up or down in front of a millimeter scale; the position of the meniscus on the scale gave the depth of the standard liquid in the tube.

The two tubes were enclosed, to prevent access of light from the side, and were slanted a little, so that the tops touched but the bottoms were about a centimeter apart; they were covered by a white card in which two small holes were made, so that on looking into the solutions the sides of the tubes could not be seen.

The whole apparatus was surrounded with ice water to prevent heat from the arc lamp (which served as source of light) from raising the temperature, and affecting the colour.

Measurements with this apparatus proved that if ferric chloride be present in sufficient excess, the depth of colour is directly proportional to the amount of acetonoxalic ester, provided that the readings are not made when the tubes are nearly empty. The following table shows the degree of accuracy attained.

In the table the first column gives the volume of F/250 acetonoxalic ester (dissolved in 1 percent alcohol);[1] the second and third, the height of the standard solution in millimeters in two sets of experiments, two settings were made in each case; while the fourth and fifth columns give the quotients, or the height in millimeters of the standard solution corresponding to 1 cc of the volumetric ester solution. When the reading is 38 or more, the quotient remains constant at 5.40 ± 0.05.

In pure solutions of acetonoxalic ester, therefore, the ferric reaction serves as basis for a satisfactory colorimetric determination; it remained to see whether any of the other chemicals present also gave a colour with iron. Acetone, or oxalic ester alone gave no colour; the sodium ethylate was neutralized before the iron was added; mixtures of sodium

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[1] Containing 0.624 gram ester per liter, or approximately one formula weight in 250 liters.

ethylate and oxalic ester gave a reddish colour, but the tint was too faint to be measured in the colorimeter.

TABLE I

Ester	Colorimeter reading		Quotient	
	Set I	Set II	I	II
4cc	21 21	— —	5.02	—
6	32.5, 32.5	— —	5.04	—
7	37.5, 38.0	38.0, 38.0	5.4	5.4
8	44.0, 44.0	43.0, 44.0	5.5	5.4
9	49.0, 49.0	49.0, 49.5	5.4	5.4
10	55.0, 52.0	55.0, 55.0	5.35	5.5
11	60.5, 60.5	60.0, 60.5	5.5	5.5
12	65.0, 66.0	65.0, 66.0	5.4	5.4

Hence 0.000624 gram acetonoxalic ester gives 5.4 mm of standard colour.

The possible formation of acetondioxalic ester had also to be reckoned with, although the conditions prescribed in the instructions[1] for preparing this compound are very different from those obtaining in my experiments. I consequently prepared a quantity of this ester, and found that with ferric chloride in aqueous-alcoholic solution it gives various shades of brown. None of this compound appears to be formed in my experiments, but in the mixtures of acetonoxalic ester with 5 percent or so of acetondioxalic ester I was unable to detect the brown colour in the presence of the red either with the naked eye, or with a pocket spectroscope.

The colorimetric determination, after addition of ferric chloride, was consequently adopted as my method of analysis, and a standard colour was prepared by making up 2 cc of an F/2 solution of acetonoxalic ester (19.5 grams crystallized ester made up to 250 cc with Squibb's alcohol) and 25 cc ferric chloride solution[2] to one-quarter liter with water. The colour of this solution faded very slowly, but to obviate the

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[1] Ber. chem. Ges. Berlin, 22, 3271 (1890).

[2] 81.3 grams of Merck's crystallized hydrate per liter.

possibility of errors from this source, the standard colour was made up fresh daily.

The Double Reading

Having thus provided myself with a method of analysis, I proceeded with the determinations of the rate at which acetone and ethyl oxalate react; but after a number of measurements had been made, I was surprised by an experiment in which the acetonoxalic ester present (measured as usual with the colorimeter) was just twice as much as could possibly be formed from the amounts of acetone and ethyl oxalate taken.

At first, of course, this looked liked a slip, but investigation showed that whenever excess of sodium ethylate had been used the readings were high. I then made a study of the reaction between sodium ethylate and my preparation of acetonoxalic ester, and found that when these two substances are brought together in equivalent quantities in absolute-alcohol solution, the mixture after neutralization with acid and addition of ferric chloride gives just twice the reading in the colorimeter that would have been obtained from the acetonoxalic ester employed without such treatment. If less than one equivalent of ethylate be added, the increase in colour is proportional to the amount added; excess of ethylate over one equivalent is without effect on the colour.

The colour matches nicely with the red of my standard solution. On dilution with water or alcohol, however, the colour fades, like that of ferric sulphocyanate, and in this respect differs from the standard.

The most remarkable thing about this new reaction, however, is that if ethyl oxalate be added to the alcohol solution after treatment with the ethylate the single, instead of the double, reading is obtained. The reactions in alcoholic solution between sodium ethylate and acetonoxalic ester, and between ethyl oxalate and the new substance are instantaneous.

Ferric Chloride and Other Keto-Esters

Compounds of ferric chloride with esters of the keto-acids have been studied by Geuther,[1] Bishop, Claisen and Sinclair,[2] Wislicenus,[3] Traube,[4] Knorr,[5] Morrel and Crofts,[6] and R. Schiff.[7] Geuther remarked the similarity between the colours produced by ferric chloride with acetacetic ester and with phenol, which he took as indicating similarity of structure between them; and, ever since, the presence or absence of the ferric reaction has been repeatedly discussed in the controversies over the enol and keto formulas for these esters, until at the present time the ferric reaction is generally accepted as the criterion for enolic constitution.

The reaction with sodium ethylate, which therefore might be interpreted as giving rise to a new enol group, seemed worth further consideration; and in reviewing the literature of acetacetic ester I found that in 1898 Robert Schiff[7] had already noted that traces of sodium ethylate enolize the keto form, in the case of the addition product of benzal-aniline and acetacetic ester, and that piperidine ketoizes the enol form; and from later experiments the author concludes that the reaction is quite general with this class of compounds.

My own investigations have shown that oxalacetic ester (prepared as described in *Liebig's Ann.*, **247**, 317) gives a red colour with ferric chloride, which is sharply *trebled* by treatment with sodium ethylate.

Acetacetic ester (Kahlbaum) gives a violet, which is unaffected by the ethylate treatment.

Methylacetacetic ester (Kahlbaum) was likewise unaffected. With regard to the "undoubling" by oxalic ester,

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[1] Arch der Pharm., **116**, 97–110.
[2] Liebig's Ann., **281**, 344.
[3] Ibid., **291**, 147 (1896).
[4] Ber. chem. Ges. Berlin, **29**, 1718 (1896).
[5] Ibid., **30**, 2387 (1897).
[6] Jour. Chem. Soc., **73**, (1898).
[7] Ber. chem. Ges. Berlin, **31**, 601, 1388 (1898).

I find that in the case of acetonoxalic ester the same result is produced by the use of ethyl acetate.

The colour produced by ferric chloride in solutions of acetacetic ester resembles the "double" colour from acetonoxalic ester and the "treble" colour from oxalacetic ester, in being partially bleached by the addition of alcohol or water. It is therefore natural to suppose that the acetacetic ester from Kahlbaum's factory is in the same state as my acetonoxalic ester after treatment with sodium ethylate.

Before leaving this subject, I propose to compare the depth of the colour produced by ferric chloride in the solutions of the different esters, and see whether from this point of view also the acetacetic ester colour is comparable with the "double" colour from acetonoxalic ester. Of course, as the red compounds are not identical in the different cases, no very sharp results can be expected; they are, however, analogous, and preliminary experiments have shown me that the colour produced by ferric chloride in solutions of resorcin is closely twice that given by an equimolar solution of phenol.

The sharp doubling of the colour produced by ferric chloride with my specimen of acetonoxalic ester after previous treatment with sodium ethylate, would seem best accounted for by my compound having mono-hydroxyl constitution,

$$CH_3.CO.CH:C(OH).COOC_2H_5 \quad \text{or} \quad CH_3.C(OH):CH.CO.COOC_2H_5;$$

Perkin[1] and Gladstone, however, have concluded both from the magnetic rotation of the plane of polarization and the refractive power of a specimen of acetonoxalic ester supplied by Claisen that the constitution of the compound is represented by the dihydroxyl formula,

$$CH_3.C(OH):C:C(OH).COOC_2H_5.$$

Since this representation does not agree so well with my experiments, I determined the index of refraction of my compound to see if the two were identical.

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[1] Jour. Chem. Soc., 61, 821 (1892).

The value given by Perkin and Gladstone for the sodium line is

$$n_D = 1.475699 \text{ at } 17°,[1]$$

experimentally I found

$$n_D = 1.4750 \text{ at } 20°.$$

This measurement, together with the agreement in melting and boiling-points, leaves little doubt that my specimen of the ester was identical with that prepared by Claisen.

Boiling at atmospheric pressure for five minutes, and subsequent cooling, did not affect the refractive index, or the depth of colour with ferric chloride.

Attempts made to isolate a sodium salt corresponding to the "double" ferric salt, have not yet led to the desired conclusion, although sodium compounds have been isolated which contain a higher percent of sodium than the normal compound, and which give a colour with ferric chloride proportional to their content of sodium.

Effect of Water and of Alcohol on the Yield of Acetonoxalic Ester

The great effect exerted by traces of water on the yield has already been referred to (p. 5); the following table gives the results of experiments carried out with alcohol to which measured amounts of water had purposely been added.

Equivalent quantities of the three reagents, *viz.*, 0.50 cc ethyl oxalate, 0.27 cc acetone, 2.10 cc alcoholic solution of sodium ethylate (1.74 normal) and 2.13 cc alcohol—making a total volume of 5.0 cc—were mixed and the reaction allowed to proceed to completion. In the first experiment Squibb's absolute alcohol was used, in the others a solution of water in alcohol; the weight and the volume percent of the water in the 5 cc of reaction mixture is given in the table. Under "yield" is entered the amount of acetonoxalic ester formed in percent of that theoretically possible.

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[1] Jour. Chem. Soc., 61, 855 (1892).

TABLE IIa

Water present		Yield
Grams	Vol. percent	Percent
0	0	96
0.0107	0.213	69
0.0146	0.291	56
0.0320	0.639	34
0.0426	0.852	20
0.0533	1.065	10
0.0639	1.278	7.5

In studying the effect of alcohol on the yield, it was, of course, impossible to keep the volume constant; addition of alcohol was therefore necessarily attended by retardation of the rate of condensation. That the yield also was reduced is shown by the experiments of the following table:

TABLE IIb

Acetone cc	Oxalate cc	Ethylate cc	Total vol.	Time	Yield Percent
0.27	0.50	2.10	2.87	1 hour	100
"	"	"	5.00	2 days	100
"	"	"	10.00	2 "	70
"	"	"	10.00	28 "	72
"	"	"	20.00	28 "	57 & 58[1]
0.54	0.50	2.10	3.14	1 hour	100
"	"	"	5.00	2 days	100
"	"	"	10.00	28 "	75 & 77
"	"	"	20.00	28 "	62
0.27	1.00	2.10	3.37	1 hour	100
"	"	"	5.00	2 days	100
"	"	"	10.00	28 "	74 & 77
"	"	"	20.00	28 "	58 & 60

The results recorded in Table II suggested the possibility that sodium acetonoxalic ester might be decomposed by alcohol, as Geuther found sodium acetacetic ester to be. The mixture whose composition is given in the first line of Table II (which gives a hundred percent yield in an hour)

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[1] Duplicates.

was accordingly made up, and after standing an hour and a half was diluted with alcohol, replaced in the thermostat (at 0° C), and analyzed after standing the time entered under "time" in Table III.

TABLE III

Volume	Time	Yield Percent
2.82 cc	0	100
5.00	11 hours	96
10.00	41 "	92
20.00	11 "	92
30.00	40 "	91
40.00	38 "	94

When the alcohol was first added, the sodium compound was stirred up with the solution by a dry rod, and the tube and contents were well shaken from time to time.

These experiments seem to show that the reaction studied in this paper is a reversible one, although it is clear that the equilibrium has not been attained in the experiments of Table III. A complete study of the reaction therefore involves measurements of the rate of condensation, the rate of alcoholysis, and the conditions of equilibrium. The present paper deals with the first of these only.

C. The Rate of Formation of Acetonoxalic Ester

The chemicals used in these measurements, and in those of Tables I, II and III, were:

Acetone.—Kahlbaum's "aus der Bisulfitverbindung."

Ethyl Oxalate, from Eimer & Amend, neutral.

Alcohol.—Squibb's absolute.

Acetonoxalic Ester, prepared as described on p. 5. Melting-point, 18° C; boiling-point, 210° C.

Ferric Chloride, Merck's C. P.

Sodium Ethylate.—For the preliminary experiments, a stock of the ethylate solution was prepared by dissolving sodium in alcohol, and kept in an atmosphere of hydrogen generated electrolytically from a solution of caustic potash. On standing, however, the solution turned brown, and gave results different from those with a fresh preparation. In the end, I found it best to make up a fresh solution daily; the concentration was determined by titration with normal sulphuric acid, using methyl orange as indicator.

Method of Working

The reagents were measured into large test-tubes (150 cc) closed with rubber stoppers, and placed in a thermostat at zero. A separate mixture was used for each analysis, for fear of introducing water. The sodium ethylate pipette was washed with water and dried with a hot air-blast before each measurement.

When it was desired to stop the reaction, a measured volume of water was added, whereupon the caustic soda (formed from the ethylate and from the sodium-acetonoxalic ester) promptly saponified the excess of oxalic ester, and was itself neutralized in the process; as one mol of the ester will thus neutralize two of the ethylate, it was not necessary to add additional ester except when an excess of ethylate had been used in making up the reacting mixture. After the caustic soda has been neutralized the ethyl oxalate is very slowly saponified, and thus makes the solution only slightly acid.

A known fraction of the aqueous alcoholic solution was then removed, mixed with 4 cc of the ferric chloride,[1] and compared with the standard in the colorimeter; enough of the reaction product was taken in each case to bring the reading between 30 and 50 mm. Two or three settings of the colorimeter were made in each case; and from three to eight samples of each reacting mixture were pipetted out and analyzed, depending on the agreement between the results, and on the ease with which I found I could decide on the end-point—that is to say, no doubt, on the state of my eyes.

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[1] See foot-note, p. 7.

The results of these rate measurements are presented in tables, at the head of each of which are given the initial quantities of the reagents in milligramme-formula-weights, and the volume of the reacting mixture; in cubic centimeter under t the duration of the reaction in hours; under x the amount of acetonoxalic ester formed in milligramme-formula-weights; and under x *per liter* the amount of acetonoxalic ester formed per liter expressed in the same units. The values of x were calculated as follows:

$$x = \frac{(\text{color reading}) \times (\text{vol. after adding water})}{(\text{vol. analyzed}) \times 5.4 \times 250}$$

In Tables IV–IX to "vol. after adding water" was 40 cc.

The experiments show that the powers of the concentrations to which the rate of condensation is proportional depend upon the degree of dilution by alcohol. In Tables IV–IX (vol. 20 cc) the rate is proportional to the first power of the concentration of the acetone, and to about the 1.2 power of the concentrations of the oxalic ester and of the ethylate. On diluting the same amounts of the three reagents to a volume of 30 cc the powers become 1, 1.75, 1.75 respectively; and on further dilution to 40 cc (Tables X–XVI) and to 50 cc (Tables XVII–XX) while still proportional to the concentration of the acetone, the rate is found to vary with the square of the concentrations of the oxalic ester and of the ethylate respectively.

This difference between the behaviour of acetone on the one hand, and that of the other two reagents on the other, lends support to Claisen's formulation of the condensation if it be supposed that the addition product assumed by him is largely dissociated in alcoholic solution. To account for the second powers of the concentrations met with at the higher dilutions, however, the addition product must be given twice the molecular weight assumed by Claisen.

Tables IV–IX give the experimental results without any attempt to represent them by a differential equation. For the experiments of Tables X–XX, however, I have calculated the velocity constants of the equations

$$dx/dt K_1(A-x)(B-x)^2(C-x)^2 - K_2x(D-x) \qquad \text{Equation 1}$$
$$dx/dt K_1(A-x)(B-x)^2(C-x)^3 - K_2x^2(D-x)^2 \qquad \text{Equation 2}$$

from each successive pair of measurements by means of the "Method of Areas."

Equation 1 gave fairly constant values for K_1 but mostly negative—and therefore impossible—values for K_2; in some cases the values of K_2 were much greater than those of K_1 although the rate of condensation is obviously much greater than that of alcoholysis.

The numbers calculated from Equation 2 are more satisfactory, and are entered in the tables; in looking them over, it must be remembered that a small change in K_1 causes a large change in K_2.

The form of these equations was suggested by the experiments of p. 13; whatever hypothesis as to the mechanism of the reaction may ultimately be adopted, the constants entered in the tables may serve as the basis of a useful interpolation formula connecting the rate with the composition of the reacting solution.

My thanks are due to Prof. W. Lash Miller, at whose suggestion this research was undertaken, and under whose supervision it was carried out. The experiments were concluded in the summer of 1906.

TABLE IV

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 20

t	Series I			Series II			Series III		
	"Vol. anal."	Readings	x	"Vol. anal"	Readings	x	"Vol. anal"	Readings	x
0.25	10.0	34.5; 34; 35.0	0.102	10.0	32; 31; 31	0.093	10	34.0; 34; 33.0	0.099
0.50	6.0	43.0; 43; 42.0	0.210	5.0	32; 32; 31	0.187	5	34.0; 34; 33.0	0.199
0.75	4.0	39.0; 41; 40.0	0.296	4.0	37; 37; 37	0.275	4	39.0; 38; 39.5	0.289
1.00	3.5	45.0; 45; 44.0	0.378	3.0	35; 35; 35	0.348	3	36.0; 36; 36.0	0.355
1.50	2.5	47.0; 48; 47.5	0.563	2.0	34; 33; 34	0.496	2	35.0; 35; 35.0	0.518
2.00	2.0	45.0; 45; 45.0	0.667	2.0	42; 42; 42	0.626	2	47.5; 48; 47.0	0.629
3.00	—	— — —	—	1.5	42; 42; 42	0.829	1	30.0; 30; 30.0	0.867
4.00	—	— — —	—	1.5	50; 51; 50	1.000	1	35.0; 35; 35.0	1.037

TABLE V

Acetone 7.4 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 20

t	Series I			Series II			Series III		
	"Vol. anal."	Readings	x	"Vol. anal."	Readings	x	"Vol. anal."	Readings	x
0.25	5	34.0; 34; 34.0	0.203	5.0	31; 31.0; 31.0	0.183	5.0	32; 32; 33.0	0.192
0.50	5	64.0; 63; 63.0	0.375	4.0	48; 49.0; 47.0	0.355	3.0	37; 38; 37.0	0.370
0.75	3	52.0; 51; 51.5	0.511	3.0	50; 49.0; 49.5	0.489	—	— — —	—
1.0	2	44.0; 45; 44.5	0.659	2.0	43; 43.0; 43.0	0.637	1.5	33; 32; 33.0	0.644
1.5	1	31.5; 31; 31.0	0.925	2.0	57; 58.0; 57.0	0.852	1.5	43; 43; 43.5	0.851
2.0	1	38.5; 39; 39.0	1.140	1.0	34; 35.5; 33.0	0.993	1.0	34; 35; 34.0	1.018
3.0	—	— — —	—	1.0	43; 42.0; 42.0	1.260	1.0	43; 43; 42.5	1.270
4.0	—	— — —	—	0.75	35; 36.0; 36.0	1.400	1.0	46; 46; 47.0	1.400

TABLE VI

Acetone 3.7 Oxalic ester 7.4 Sodium ethylate 3.7 Vol. 20

t	Series I			Series II			Series III		
	"Vol. anal."	Readings	x	"Vol. anal."	Readings	x	"Vol. anal."	Readings	x
0.25	4	33.0; 33; 32.5	0.243	5.0	38; 38; 37.5	0.223	5.0	40; 40; 40.0	0.237
0.50	3	43.0; 43; 44.0	0.429	4.0	59; 59; 59.0	0.437	4.0	60; 60; 60.5	0.445
0.75	2	43.0; 43; 44.0	0.642	3.0	68; 67; 66.0	0.661	3.0	66; 67; 66.0	0.656
1.0	2	54.5; 55; 55.0	0.811	2.0	58; 57; 57.0	0.851	2.0	56; 56; 56.0	0.830
1.5	1	36.0; 37; 37.0	1.089	1.5	56; 56; 56.5	1.110	1.5	59; 58; 58.0	1.155
2.0	1	46.0; 46; 45.0	1.355	1.0	46; 46; 46.0	1.360	1.0	47; 47; 48.0	1.400
3.0	—	— — —	—	1.0	54; 54; 53.0	1.648	1.0	55; 55; 55.0	1.629
4.0	—	— — —	—	0.75	42; 42; 42.0	1.679	0.75	43; 43; 43.0	1.702

TABLE VII*

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 7.4

t	Series I			Series II			Series III		
	"Vol. anal."	Readings	x	"Vol. anal."	Readings	x	"Vol. anal."	Readings	x
0.25	3	50; 49.0; 49.5	0.244	3	48.0; 48; 48.0	0.237	3	46.5; 47; 46.0	0.229
0.50	2	62; 62.5; 63.0	0.463	2	65.0; 65; 65.0	0.482	2	60.0; 60; 60.0	0.445
0.75	1	40; 40.0; 40.0	0.593	1	37.5; 38; 38.0	0.555	1	37.5; 38; 38.0	0.555
1.0	1	55; 55.0; 55.0	0.815	1	51.0; 50; 50.0	0.750	1	47.0; 48; 48.0	0.704
1.5	0.75	50; 50.0; 49.5	0.981	0.75	47.0; 47; 46.5	0.926	0.75	46.0; 47; 47.0	0.926
2.0	0.75	56; 56.0; 56.5	1.110	0.75	58.0; 58; 58.5	1.148	0.5	39.0; 39; 39.5	1.160
3.0	—	— — —	—	0.5	50.0; 50; 50.0	1.480	0.5	51.0; 52; 51.0	1.526
4.0	—	— — —	—	0.5	62.0; 61; 62.0	1.810	0.5	62.0; 61; 61.0	1.810

* On account of the double reading (see p. 8) in Tables VII, XIII and XX the readings have been halved in calculating x. See also Table XIII*b*.

TABLE VIII

Acetone 11.1 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 20

t	"Vol. anal."	Readings	x
0.25	4.0	42.0; 42.0; 42.0	0.311
0.50	3.0	52.5; 53.0; 52.0	0.518
0.75	2.0	45.5; 45.5; 45.5	0.674
1.0	1.5	41.5; 42.0; 42.0	0.822
1.5	1.0	36.0; 36.0; 36.0	1.067
2.0	0.75	32.0; 31.0; 31.5	1.245
3.0	0.75	40.0; 41.0; 40.0	1.595

TABLE IX

Acetone 3.7 Oxalic ester 11.1 Sodium ethylate 3.7 Vol. 20

t	"Vol. anal."	Readings	x
0.25	3.0	34.0; 34.0; 35.0	0.341
0.50	2.5	52.0; 52.0; 52.0	0.616
0.75	1.25	40.0; 39.0; 40.0	0.939
1.0	1.0	40.0; 40.0; 39.5	1.178
1.5	0.75	40.0; 41.5; 41.0	1.622
2.0	0.6	39.5; 40.0; 40.5	1.970
3.0	0.5	38.5; 39.0; 39.0	2.290

TABLE X

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 40

t	x	x per liter	$K_1 \times 10^{12}$
4.0	0.069	1.725	—
6.5	0.115	2.875	68
16.0	0.272	6.80	74
24.0	0.385	9.525	67
35.0	0.500	12.50	69
40.0	0.563	14.075	79
48.0	0.593	22.05	66
72.0	0.882	31.00	80
120.0	1.240	37.00	80
192.0	1.481	47.00	86
—	1.888	—	—
		Average	74

TABLE XI

Acetone 7.4 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 40

t	x	x per liter	$K_1 \times 10^{13}$	K_2
4	0.122	3.05	—	—
8	0.244	6.10	—	—
16	0.467	11.67	57	11×10^{-13}
24	0.607	15.17	56	36×10^{-13}
35	0.741	18.52	48	13×10^{-13}
40	0.800	20.00	42	10×10^{-13}
48	0.860	21.50	40	—

TABLE XII

Acetone 3.7 Oxalic ester 7.4 Sodium ethylate 3.7 Vol. 40

t	x	x per liter	$K_1 \times 10^{13}$	K_2
4	0.250	6.25	—	—
8	0.459	11.47	72	—
16	0.778	19.45	80	14×10^{-13}
24	0.964	24.10	78	11×10^{-13}
35	1.112	27.80	73	7×10^{-13}
40	1.169	29.22	63	5×10^{-13}
48	1.259	31.47	69	4×10^{-13}
72	1.511	37.77	64	3×10^{-13}
120	1.837	45.92	55	—
240	2.192	54.80	—	—
—	2.222	55.50	—	—

TABLE XIII

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 7.4 Vol. 40

t	x	x per liter	$K_1 \times 10^{13}$	K_2
4	0.280	7.00	—	—
8	0.426	10.65	73	—
16	0.611	15.27	58	20×10^{-13}
24	0.778	19.45	53	4×10^{-13}
35	0.964	24.10	52	3×10^{-13}
40	1.037	25.92	55	3×10^{-13}
48	1.111	27.77	52	4×10^{-13}
72	1.288	32.20	49	3×10^{-13}
120	1.518	37.95	42	3×10^{-13}
168	1.741	43.92	41	2×10^{-13}
192	1.837	45.92	41	—
—	2.185	54.62	—	—

TABLE XIV

Acetone 11.1 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 40

t	x	x per liter	$K_1 \times 10^{13}$	K_2
4	0.177	4.42	41	—
8	0.311	7.77	56	—
16	0.591	14.77	61	—
24	0.829	20.72	63	—
35	1.036	25.90	70	20×10^{-13}
40	1.118	27.95	77	—
48	1.215	30.37	74	—
		Average	64	

TABLE XV

Acetone 3.7 Oxalic ester 11.1 Sodium ethylate 3.7 Vol. 40

t	x	x per liter	$K_1 \times 10^{13}$	K_2
4	0.433	10.82	—	—
8	0.813	20.32	60	—
16	1.301	32.52	60	—
24	1.481	35.02	59	—
35	1.735	43.37	69	—
48	1.895	47.37	68	5×10^{-13}
72	2.104	52.60	63	1×10^{-13}
120	2.385	58.62	67	—

TABLE XVI

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 11.1 Vol. 40

t	x	x per liter	$K_1 \times 10^{13}$	K_2
4	0.444	11.00	56	—
8	0.814	20.35	63	—
16	1.259	31.47	74	13×10^{-13}
24	1.408	35.20	63	—
35	1.660	41.50	63	—

TABLE XVII

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 50

t	x	x per liter	$K_1 \times 10^{13}$	K_2
12	0.145	2.90	38	320×10^{-13}
24	0.288	5.66	37	—
36	0.429	8.58	45	73×10^{-13}
48	0.518	10.36	45	93×10^{-13}
72	0.711	14.22	46	33×10^{-13}
96	0.837	16.74	47	40×10^{-13}
120	0.922	18.44	46	33×10^{-13}
144	1.000	20.00	46	31×10^{-13}

TABLE XVIII

Acetone 7.4 Oxalic ester 3.7 Sodium ethylate 3.7 Vol. 50

t	x	x per liter	$K_1 \times 10^{13}$	K_2
12	0.244	4.88	34	—
24	0.459	9.18	37	15×10^{-13}
36	0.615	12.30	36	5×10^{-13}
48	0.741	14.82	33	—
72	1.007	20.14	38	3×10^{-13}
96	1.155	23.10	38	3×10^{-13}
120	1.260	25.20	38	3×10^{-13}
144	1.518	30.36	—	—

TABLE XIX

Acetone 3.7 Oxalic ester 7.4 Sodium ethylate 3.7 Vol. 50

t	x	x per liter	$K_1 \times 10^{13}$	K_2
12	0.377	7.54	27	—
24	0.703	14.06	30	—
36	0.941	18.82	33	10×10^{-13}
48	1.081	21.62	32	9×10^{-13}
72	1.260	25.20	29	4×10^{-13}
96	1.452	29.04	28	2×10^{-13}
120	1.592	31.84	30	4×10^{-13}
144	1.604	32.08	—	—

TABLE XX

Acetone 3.7 Oxalic ester 3.7 Sodium ethylate 7.4 Vol. 50

t	x	x per liter	$K_1 \times 10^{13}$	K_2
12	0.400	8.00	30	1×10^{-13}
24	0.702	14.04	30	—
36	0.923	18.46	32	9×10^{-13}
48	1.080	21.60	30	2×10^{-13}
72	1.306	26.02	25	1×10^{-13}
120	1.581	31.62	26	1×10^{-13}
144	1.702	34.04	27	1×10^{-13}

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ELECTROLYTIC SEPARATION OF SILVER AND COPPER

BY H. W. GILLETT

Root[1] gives the following decomposition voltages in ammoniacal tartrate solution at 60°, Ag 1.0 volt, Cu 1.65 volts, H 1.9 volts. There is evidently some unknown variable because I obtained the lower values of about 0.65 volt for silver and about 1.35 volts for copper. At 20° the values were 0.95 volt for silver and 1.8 volts for copper. These results made it seem probable that a fairly rapid constant-voltage separation of silver from copper might be effected in ammoniacal tartrate solution.

It was found by preliminary experiments that a good deposit of silver was not obtained from an ammoniacal tartrate solution even with a current density as low as 0.15 amp/dm^2 unless one of the electrodes was rotated rapidly. If either cathode or anode were rotated rapidly enough, a current density of 0.45 amp/dm^2 could be used at 70°. In order to keep the current density low, the runs were made with a Classen dish as cathode and a rotating Classen disc as anode. The silver was determined by weighing and also by titration of the dissolved deposit, using ammonium sulphocyanate with ferric alum as an indicator.

The following three runs were made at 70°, the silver and copper being added in the form of nitrates. The solutions 0.1032 gram Ag, 0.1161 gram Cu, 7 grams tartaric acid, and 25 cc ammonia (sp. gr. 0.9) per 120 cc. The voltages were 1.0, 1.35 and 1.2 and the amounts of silver found were 0.1033 gram, 0.1026 gram and 0.1024 gram. Runs were next made at 20°, the solutions containing 7 grams tartaric acid and 25 cc ammonia per 120 cc.

A very rapid rotation of the anode is necessary, especially at the lower temperature. If this precaution is not observed

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[1] Jour. Phys. Chem., 7, 428 (1903).

the deposit will not adhere satisfactorily and too little silver will be found.

TABLE I

Voltage	Grams Cu	Grams Ag	Grams Ag found
1.35–1.55	0.1161	0.1421	0.1417[1]
1.35–1.55	0.1161	0.1421	0.1424
1.35–1.60	0.0290	0.1421	0.1429
1.35–1.60	0.1161	0.0355	0.0347
1.35–1.53	0.1161	0.0355	0.0344
1.35–1.53	0.1161	0.0355	0.0354
1.35–1.53	0.1161	0.0355	0.0352

It seemed desirable also to determine the copper left in the solution. It was hoped that this could be done by raising the voltage, but the copper deposit was bad at all current densities. After a number of experiments I fell back on the standard method: acidify with HCl, heat nearly to boiling, precipitate the copper by H_2S, filter off the copper sulphide, dissolve in nitric acid containing a little sulphuric acid, filter from the sulphur, and electrolyze with a rapidly rotating anode and a current density of 2–4 amp/dm^2.

This work was suggested by Professor Bancroft and was carried out under his supervision.

Cornell University.

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[1] Non-adherent, owing to the anode not having been rotated sufficiently rapidly.

ELECTROLYTIC DETERMINATION OF MINUTE QUANTITIES OF COPPER[1]

BY E. E. FREE

The determination of quantities of copper less than one milligram cannot be carried out satisfactorily by the ordinary procedure of electrolytic analysis because of the impossibility of weighing with sufficient accuracy the dishes or other cathodes usually employed. Phelps[2] avoids this difficulty by precipitating the copper electrolytically, dissolving the deposit and estimating it colorimetrically. By the use, however, of a small electrode the colorimetric determination may be dispensed with and the copper weighed directly as deposited, a fair degree of accuracy being obtainable with quantities of copper as small as 0.05 milligram. The electrode is made from a small piece of platinum wire bent into a spiral with one end extending along its axis. It is supported in the bath by wrapping this free end four or five times about a hook of heavy platinum wire. If the hook be straight and slightly tapered toward the point the electrode may be easily attached and removed and makes perfect contact with the hook. The electrode used by the writer weighed about 0.3 gram.

The extraction and concentration of the copper are carried out by the usual methods. The electrolysis may be made in either nitric or sulphuric acid solution, low currents being used on account of the small cathode area. The writer uses 2 percent to 4 percent nitric acid and a few drops of sulphuric acid in about 25 cc solution and electrolyzes over night with about 1.8 volts and 0.01 ampere. The containing dish serves as anode. When the deposition is finished the electrolyte is washed out with a siphon or sucking-bottle without breaking the current. The electrode is grasped with a pair of small forceps, removed from the hook, washed successively in water, alcohol and ether, dried over sulphuric acid and weighed with great accuracy on a button balance.

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[1] Read at New York meeting of American Electrochemical Society.

[2] Jour. Am. Chem. Soc., 28, 368 (1906).

The copper is then removed by nitric acid and the electrode washed, dried and weighed as before. The difference gives the weight of the copper. Following are some results, the first four obtained by electrolyzing a solution of known strength, the last two by redissolving the copper from one precipitation and reprecipitating on another electrode.

No.	Copper present, Mgs	Copper found, Mgs
1	0.529	0.509
2	0.492	0.498
3	0.556	0.558
4	0.499	0.500

	Copper found	
No.	1st precipitation, Mgs	2nd precipitation, Mgs
5	0.092	0.104
6	0.348	0.344

Uniformly good deposits are obtained from solutions containing nothing but copper salts and acids. If, however, compounds of carbon or of platinum (derived from platinum dishes during the preliminary treatment) are present in the electrolyte the deposit will be black and loosely adherent, owing to contamination with these elements,[1] and the results will be high. Organic matter dissolved in the disintegration of a filter paper by nitric acid will in this way seriously interfere with the obtaining of good deposits. The difficulty may be avoided by making a preliminary (electrolytic) precipitation on a platinum dish in the usual way, dissolving the deposit and reprecipitating on the spiral electrode as above. The carbon and platinum remain undissolved on the first dish, and the electrolyte for the second precipitation is quite pure.

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[1] The precipitation of carbon during electrolysis has recently been investigated by Blum & Smith. Proceedings Am. Philosophical Soc., 46, 60 (January-March, 1907).

NON-MISCIBILITY AND THE MASS LAW

BY WILDER D. BANCROFT

If we have two liquids A and B reacting to form a compound AB, and if there are no disturbing factors, the reversible equilibrium in the liquid phase should be described by the equation

$$Kx = yz,$$

where x, y, and z are the volume concentrations of the substances AB, A and B respectively. We will now consider the effect of the assumption that A and B are non-miscible liquids, each one being miscible in all proportions with the compound AB. This case can be realized approximately with the system chloral hydrate, chloral and water. Above the melting-point chloral hydrate is miscible in all proportions with either chloral or water. On the other hand, chloral and water form two liquid layers. I know of no measurements which show to what extent the two are miscible. This is, however, for the moment an unimportant detail.

If the components A and B are non-miscible each will make the other less soluble in the mixture and each will therefore increase the chemical potential μ of the other.[1] Since the condition for equilibrium[2] is that

$$\mu_x = \mu_y + \mu_z$$

an increase in the chemical potentials of one of the reacting systems will displace the equilibrium and will be equivalent to an increase in the concentrations. Incidentally, it may be mentioned that making A and B non-miscible lowers the vapor pressure[3] of the compound AB and therefore decreases the chemical potential μ_x. The two effects therefore work in the same direction and the qualitative result of our assumption is a decrease in the effective concentration of the undissociated compound with a resulting forcing-back of the percentage dissociation.

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[1] Miller: Jour. Phys. Chem., 1, 633 (1907).

[2] Gibbs: Thermodynamische Studien, 112.

[3] McIntosh: Jour. Phys. Chem., 1, 474 (1907).

Putting this in another form, we see that making the two components A and B non-miscible is equivalent to increasing the apparent values of y and z, and to decreasing the apparent value of x. If the experimentally determined values of the concentrations are not the values to be used in calculating the equilibrium relations, we may get unexpected and disconcerting results if we do not take this into account.

We do not know as yet, the way in which the chemical potentials of A and B are changed quantitatively by the introduction of the phenomenon of non-miscibility, but we can work out the effect of certain arbitrary assumptions. We will let x, y, and z be as before the analytically determined concentrations of AB, A and B respectively and we will let X, Y and Z be the theoretical concentrations, due to the assumed non-miscibility of the components A and B. Our equation for equilibrium then becomes:

$$\mathrm{KX} = \mathrm{YZ}.$$

To simplify the problem still further, we will ignore the change in the chemical potential of the compound, which means that we write

$$x = \mathrm{X}.$$

This probably involves only a slight error for cases in which the compound does not dissociate to any great extent when the components A and B are present in equivalent quantities.

In the discussion that follows I am considering the chemical potentials of the components in the vapor phase as given by the equations,

$$\mu_\mathrm{A} = \mathrm{RT}(\log p_a + \mathrm{C}_1)$$
$$\mu_\mathrm{B} = \mathrm{RT}(\log p_\mathrm{B} + \mathrm{C}_2).$$

Case I.—The increase in the chemical potential of either component may be a constant and independent of the absolute concentration of either. If these be true we shall have:

$$\mathrm{Y} = k_1 y$$
$$\mathrm{Z} = k_2 z$$
$$\frac{\mathrm{K}}{k_1 k_2} x = yz.$$

Under these circumstances we shall have the same form of equation whether we use the theoretical or the analytical concentrations, the only difference being that the equilibrium constant will change from K to K/k_1k_2. While this case is hypothetically possible, it is not a case which occurs experimentally. We know that experimentally the partial pressure of one of the components changes continuously with addition of the other component when the two components are non-miscible.

Case II.—The increase in the chemical potential of either component may be directly proportional to the chemical potential of the other component. If this be true we shall have:[1]

$$Y = yz^n$$
$$Z = y^m z$$
$$Kx = y^{1+m}z^{1+n}.$$

Under these circumstances we shall have an entirely different form of equation. If $m = 1$, for instance, we should conclude that the component had a molecular weight equal to half the formula weight whereas that would not be the case at all. If m and n were fractions, we should get slight variations from the expected formula which we should interpret as due to partial polymerization of the compound, to variations from the gas laws, or to some other natural but inapplicable cause.

While *Case II* is a more plausible one than *Case I*, it is not very probable that the change of the vapor pressure of one of the components is independent of the absolute concentration of that component even though it may be approximately true between narrow limits.

Case III.—The increase in the chemical potential of either component may be inversely proportional to the chemical potential of that component and directly proportional to the chemical potential of the other component. If this be true we shall have:

$$Y = \frac{yz^n}{y^p}.$$
$$Z = \frac{y^m z}{z^q}.$$
$$Kx = y^{1+m-p}z^{1+n-q}.$$

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[1] The K in this equation is not the same as in the preceding one since it contains m and n as exponential functions.

Since m, n, p, and q are constants, *Case II* and *Case III* would both give an equation of the general form:

$$Kx = y^a z^b$$

Where $a = 1 + m$ and $b = 1 + n$ for *Case II* while $a = 1 + m - p$ and $b = 1 + n - q$ for *Case III*. Since the equations for *Case II* and *Case III* have the same general form, the same general remarks apply with one exception. Under *Case II* the exponents cannot be unity. Under *Case III* it is conceivable that $m = p$ and that $n = q$. If so the equation for equilibrium would have the form

$$Kx = yz.$$

Under these conditions the effect due to the non-miscibility disappears so far as the concentrations of the components is concerned. Systems coming under this head could be distinguished, however, from systems involving complete miscibility by varying the concentrations over such a range that we should have to drop the simplifying assumption that $x = X$.

Case IV.—The change in the chemical potential of either component is some other function of the chemical potentials of the components than that postulated under *Case III*. Until one assigns a value to the unknown function, one cannot say what form the equation of equilibrium will take, but it is only under special conditions that the effect due to the non-miscibility of the components will disappear as far as the two components are concerned, and there is no reason to suppose that it will ever disappear if one takes into account the difference between the analytical and the theoretical concentration of the compound.

If we exclude *Case I* as impossible, we reach the conclusion that the mass law formula, as usually applied, will never describe the equilibrium in a single liquid phase for a dissociating compound when the dissociation products are non-miscible, though each is miscible in all proportions with the compound.

The case where the components are partially miscible is of course intermediate between the two extremes of complete miscibility and complete non-miscibility. There is therefore nothing to be gained by discussing such systems in detail before we have experimental data concerning them.

This matter of obtaining experimental data is a serious one. In chloral hydrate we have a substance which dissociates somewhat in the liquid phase at suitable temperatures. In butyl-chloral hydrate we have a substance which dissociates a good deal more. The problem is how to determine the degree of dissociation with accuracy. So far I have not been able to devise any method of analysis which would be satisfactory. I am publishing this paper, partly in the hope that some one else may display greater ingenuity.

Having shown the necessity for modifying the mass law formula when we postulate non-miscibility in a two-component system, it may be well to consider what may happen in three-component systems. The simplest form of this is a dissociating compound for which the mass law applies and a solvent with which one of the components is non-miscible. Let us suppose that the component A is non-miscible with the solvent S and that the solution is so dilute that we may treat the precipitating effect of the solvent as practically constant. If the increase in the chemical potential of the component A is directly proportional to the chemical potential of the solvent and inversely proportional to the chemical potential of component A we shall have

$$Y = \frac{ky}{y^n}$$

where *k* is the factor due to the chemical potential of the solvent. The equation for equilibrium therefore becomes

$$Kx = ky^{1-n}z,$$

and we see that the dissociation is not described by the simple mass law formula.

We can next consider a three-component system in which a metathetical reaction takes place according to the equation

$$AB + CD = AD + BC.$$

The normal equation for equilibrium will be

$$Kwx = yz,$$

where w, x, y and z are the volume concentrations of the four constituents. We will now postulate that AD and BC are practically non-miscible, and that each is miscible in all proportions with AB and BC. In that case we shall get special exponents for y and z even without considering w and x. In order to consider the changes in w and x, we should have to know how the chemical potentials of a varying mixture of AB and BC change with varying absolute and relative amounts of AD and BC. This cannot be done at present, but we see that there will be less formation of AD and BC if these substances are non-miscible than would be the case if they were completely miscible. We also see that the simple mass law formula will not describe the equilibrium relations accurately. To a certain extent the ester formation comes under this head, because ethyl acetate and water are only miscible to a limited extent. It may therefore be asked how it happens that the mass law formula appears to describe the facts so well. The answer is not hard to find. In the first place only a relatively small portion of the equilibrium field has been worked over. In the second place the work has been done either with alcohol or acetic acid in excess, or with water in very large excess. In other words, the experimenters have always kept well away from the saturation point where the deviations from the simple formula would be the most marked. It would not be safe to say that the remarkable results obtained by Price[1] in his work on the equilibrium between ethyl alcohol and hydrochloric acid were due to limited solubility, but it is worthy of notice that marked discrepancies between theory and experiment do occur in a system where the appearance of a second liquid layer has to be guarded against.

The general result of this investigation is that the simple mass law formula will not describe the equilibrium in any case in which the liquid phase contains two substances which are more or less completely non-miscible.

Cornell University

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[1] Jour. Chem. Soc., 79, 303 (1901).

THE RELATION OF ELECTROPLATING TO ELECTROLYTIC ANALYSIS

BY WILDER D. BANCROFT

The ideal solution for the plater is one from which he can precipitate the metal quantitatively in as nearly an amorphous form as possible and in which the anode will dissolve quantitatively. The two requisites then are a very finely crystalline deposit at the cathode and a practically constant composition of the solution. The analyst does not require so finely crystalline a deposit at the cathode, though he is glad to get it. He uses an insoluble anode and consequently is not necessarily limited in his choice of an acid radical. He does not get and does not expect to get one hundred percent current efficiency at the cathode. In these three respects he demands less than the plater. On the other hand, the analyst must get a good deposit from a solution of changing concentration down to the point at which no metal remains in solution. He must not only get the last trace of the metal out of the solution but he must precipitate it in a weighable adherent form while there is a copious evolution of hydrogen going on. In this respect the analyst's requirements are much more rigid than those of the plater. Since the analyst has to weigh the deposit, he cannot improve its quality by adding a colloid to the solution as may be done by the plater.

If a plating bath will give a good deposit for any and all concentrations of the metal, it may be used as a solution in which electrolytic analysis is carried on. If a solution for electrolytic analysis gives a sufficiently fine-grained deposit and if the anode will dissolve practically quantitatively in it, such a solution may be used as a plating bath. We should therefore expect to find that under certain circumstances the same solutions are used both for electrolytic analysis and for plating. We should further expect that in some cases the two sets of solutions will differ and that the reason for the difference will lie in the non-fulfilment of one or more of the requirements just specified. The object of this paper is to show in how far actual practice coincides with the theoretical conclusions.

In a previous paper[1] I have shown that the essential thing in securing a good metallic deposit is to prevent the precipitation of a salt of the metal with the metal. Whenever the oxide, hydroxide, cyanide or other salt separates on the cathode we invariably get a spongy deposit. Consequently any useful additions to the plating bath, which are not for the purpose of increasing the fineness of the crystals or of regulating the acidity, must consist of substances which dissolve the oxide, hydroxide, cyanide, or whatever the disturbing salt may be. In the deposition of zinc the addition of sulphuric acid, potash, ammonium chloride, ammonium sulphate, aluminum sulphate, potassium cyanide or acid potassium oxalate has been recommended. The first four dissolve zinc hydroxide and the potassium cyanide dissolves zinc cyanide. Of the substances added to nickel baths, sulphuric acid, ammonia and ammonium salts dissolve nickel hydroxide and potassium cyanide dissolves the cyanide. Sodium bicarbonate and boric acid serve to regulate the acidity. In lead baths acetic acid, potash, sodium nitrate and fluosilicic acid dissolve lead hydroxide though by no means equally well or equally rapidly. Sulphuric acid, potash, sodium phosphate, and ammonium oxalate dissolve stannous and stannic acids while ammonium sulphide dissolves the sulphide. Sulphuric acid, ammonia, alkaline tartrate, and ammonium oxalate dissolve cuprous oxide while potassium cyanide dissolves the cyanide. Nitric acid and ammonia dissolve freshly precipitated silver oxide; ammonia dissolves silver chloride; potassium cyanide dissolves silver cyanide; while silver iodide is soluble in potassium iodide. Gold cyanide is soluble in potassium cyanide and gold sulphide in sodium sulphide. The oxides of gold are soluble in bisulphide, thiosulphate and sulphocyanate solutions. A phosphate solution also has a solvent action.[2]

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[1] Jour. Phys. Chem., 9, 277 (1905).

[2] Cf. Becquerel: Phil. Mag. [5] 8, 136 (1879).

While we cannot at present predict whether one metal will give larger crystals than another when precipitated electrolytically from the sulphate solution for instance, we can tell how the size of the crystals will vary for any given metal with varying conditions of precipitation. In the paper already referred to I have shown that we may consider the electrolytic precipitation of a crystalline metal as governed by the general laws of crystallization and that the conditions favoring a nearly amorphous precipitate are high potential difference between metal and solution, high current density, low temperature, and presence of a colloid which migrates to the cathode.[1] Since platers do not stir their solutions to any extent, high current densities are not possible, and it is necessary to use solutions that give a finely crystalline deposit at moderate current densities. By using a dilute solution one can get smaller crystals than with a concentrated solution but as the conductivity of a dilute solution is low, the tendency to tree is greater and there is no real gain. If we take into account the danger of impoverishment at the cathode, there is a great disadvantage in the use of dilute solutions and, as a matter of fact, they are not used. We can get a greater difference of potential between metal and solution without any corresponding decrease of conductivity by using a complex salt of the metal to be deposited. If we take potassium silver cyanide for instance we may have a high absolute concentration of silver together with a low concentration of silver as ion. The conductivity of the solution is almost infinitely higher than that of a silver nitrate solution, having the same concentration of silver as ion and the danger of treeing is correspondingly reduced. As a matter of fact we do get a beautiful deposit of silver from a cyanide solution while that from a nitrate solution is so coarsely crystalline under ordinary circumstances as to be worthless to the plater. Another well-known advantage of using a complex salt is the way in which it minimizes the danger of spontaneous precipitation in the plating of baser metals. While the use of colloids is not a regular thing among platers we know that the

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[1] Cf. Müller and Bahntje: Zeit. Elektrochemie, 12, 317 (1906).

addition of a little gelatine has a wonderful effect with zinc, lead, tin, copper and silver.

In plating with copper, practically only two solutions are used, a cyanide solution and a solution of copper sulphate acidified with sulphuric acid. The deposit from the cyanide solution is finer than that from the sulphate solution; but as the deposit from the latter is fine enough, the sulphate solution is used almost exclusively. The cyanide solution is useful as a striking bath; but it is more expensive, more dangerous, and has a higher resistance. An alkaline tartrate solution has also been recommened for plating but has not come into general use.

Copper can be precipitated electrolytically from almost any solution. It has been precipitated quantitatively from acidified sulphate, acidified ammonium oxalate, acidified phosphate, ammoniacal ammonium nitrate, cyanide, and other solutions. Most analyses are made in an acidified copper sulphate solution, while the cyanide is used when one starts with copper sulphide. The two plating solutions are therefore identical in nature with two of the solutions used for electrolytic analysis. The differences in composition are natural ones when we keep in mind the differences in the ends to be obtained. In the plating solution the sulphuric acid serves the double purpose of preventing the precipitation of cuprous oxide and of increasing the conductivity of the solution. There is therefore no object in keeping the sulphuric acid content down to a minimum and it may run anywhere from four percent to twelve percent or even more. On the other hand, with so much free acid it would be difficult to get the last traces of copper out, and the solution for electrolytic analysis contains only a little free acid at the start. This free acid is usually nitric acid because there is danger of reducing sulphuric acid to hydrogen sulphide during the last portion of the run when one is really electrolyzing a sulphuric acid solution with a copper cathode. The nitric acid prevents this reduction, being itself reduced to ammonia. In the plating bath there is always plenty of copper sulphate in solution and consequently there is no danger of any reduction of the sulphuric acid.

The only difference between the cyanide plating bath and the cyanide analytical bath is that the initial ratio of cyanide to copper may be lower in the latter because the anode does not dissolve. It is not necessary that the ratio of cyanide to copper should be lower in the analytical solution than in the plating bath because the cyanide is oxidized at the platinum anode and can therefore be brought to any desired concentration by prolonging the electrolysis sufficiently. It is pretty wasteful, however, to add more cyanide than is necessary merely for the sake of decomposing it afterwards. In any case most of the cyanide must be decomposed if all the copper is to be precipitated[1] at 20°.

Doubtless many of the other analytical baths could be used for copper plating. Curry[2] has shown that a copper anode dissolves quantitatively in an acidified ammonium oxalate bath. Since such a bath has apparently no especial advantage as a plating bath over the two standard ones,[3] there is no reason why it should come into use. The same reasoning applies to the acidified phosphate bath, while in the ammoniacal nitrate solution it is doubtful whether the current efficiency at the cathode approximates one hundred percent.

The cyanide solution is the only one in use in plating silver, though an iodide solution has been recommended highly. A good deposit can be obtained from the cyanide for all concentrations of silver and consequently the cyanide solution can be and is used in the electrolytic determination of silver. For analytical purposes the nitrate solution is also used, but the deposit is so coarsely crystalline that it is entirely unsuitable for plating purposes. A good plating deposit can be obtained from the nitrate solution by using high current densities and a rapidly rotating cathode,[4] but this would not be practicable in commercial practice. A good deposit can

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[1] Cf. Root: Jour. Phys. Chem., 7, 461 (1903).

[2] Jour. Phys. Chem., 10, 489 (1906).

[3] It may be useful as a bronzing bath. Cf. Curry: Jour. Phys. Chem., 10, 515 (1906).

[4] Snowdon: Jour Phys. Chem., 9, 392 (1905).

also be obtained by adding gelatine to the nitrate solution. This is in actual use at the Philadelphia Mint in the electrolytic refining of silver by the Moebius process, but I do not know of its use in any plating establishment.

The plating baths for gold all contain cyanide, ferrocyanide, thiocyanate, thiosulphate or bisulphite. Of these, the cyanide bath is by far the most important. For analytical purposes the solutions in use contain potassium cyanide, potassium sulphocyanate and sodium sulphide respectively. I cannot find any record of a sulphide bath having been used for plating purposes, and it seems not improbable that a gold anode does not dissolve readily in such a solution. There is also a possible danger of forming a film of sulphide on the surface of the metal which is to be plated. Either of these would prevent the use of the sulphide bath for plating purposes. Special experiments are necessary to show whether these suggested objections are real or imaginary ones.

While on the subject of gold-plating there is a passage from McMillan's book which I should like to quote:[1]

"A current which is too strong will, of course, deposit the gold as a black powder; but within the limits between which coherent and adhesive deposits are yielded, a stronger current produces a deeper coloured coating than a weak current. Hence, speaking generally, any influence which tends to increase the current-volume gives rise to a metal possessing a warmer hue. A feeble current, a small anode, and a cold solution, alike, give, pale yellow deposits; but a stronger battery, an increase of anode-surface (and hence less resistance), or warming the liquid, increase the current-strength, and a deeper yellow tone prevails. Motion imparted to the pieces also causes the production of a lighter colour."

No explanation was offered by McMillan, but it all becomes clear if we may postulate that gold has a warmer color the more finely crystalline it is. Higher current density would give smaller crystals and therefore a warmer color. Stirring

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[1] McMillan: "A Treatise on Electrometallurgy," 2nd edition, 225.

the solution prevents impoverishment at the cathode and therefore keeps the potential difference down somewhat, thereby causing an increase in the size of the crystals and the consequent production of a lighter color. Raising the temperature would in itself increase the size of the crystals, but the increase in the current density may more than neutralize that tendency. The hypothesis could be tested by examining the samples of gold-plating under the microscope or by making runs with the same current density at two different temperatures and noting the differences in shade, if any. In support of this hypothesis is the fact[1] that metallic gold can be precipitated in a dilute liquid in so fine a state that it remains suspended, and under these circumstances it appears by reflected light, of a purple-red, whilst by transmitted light it assumes a blue color."

While not strictly germane to the subject of this paper, there is a quotation from Roseleur[2] which calls attention to a theoretical difficulty which has now disappeared. "It is a remarkable phenomenon that solutions of cyanides, even without the action of the electric current, rapidly dissolve in the cold, or at a moderate temperature, all the metals, except platinum, and that at the boiling-point they have scarcely any action upon the metals." The explanation of this is that potassium cyanide forms complex salts with the cyanides of the metals at ordinary temperatures and that these complex salts break down more and more with rising temperature. Root[3] found that, in fourth-normal cyanide solution and 0.2 g metal per 200 cc solution, cadmium precipitates before copper at 20° while the reverse is the case at 60°. With double-normal potassium cyanide solution and 0.2 g metal per 200 cc solution, mercury and cadmium precipitate before silver at 20° and silver before mercury and cadmium at 60°.

The plating baths for nickel consist of nickel sulphate and ammonium sulphate in varying proportions with and without

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[1] Roscoe and Schorlemmer: "Treatise on Chemistry," 2^{II}, 373.

[2] Watt and Philip: "Electro-Plating and Electro-Refining, 182."

[3] Jour. Phys. Chem., 7, 461 (1903). Cf. also Foerster: Zeit. Elektrochemie, 13, 561 (1907).

additions of ammonia, citrate, tartrate, etc. Pfanhauser[1] recommends the use of sodium salts instead of ammonium salts. Since nickel anodes do not dissolve readily in sulphate solutions, pure anodes are practically never used commercially. An alloy of iron and nickel is used[2] instead with the corresponding disadvantage that the plating deposit contains iron also. Electroplating with nickel is, therefore, not strictly comparable with electroplating with copper, silver or gold, and would come under the same category as the electrodeposition of brass, except that apparently no one knows or cares how much iron is precipitated with the nickel.[3] If the solution contained a chloride, the whole difficulty would disappear.

Nickel is determined electrolytically in an ammoniacal sulphate solution, in ammonium oxalate solution, in cyanide solution, and in an ammoniacal phosphate solution. Nickel cannot be determined electrolytically in a straight ammonium sulphate solution because the solution soon becomes so acid that it is impossible to get any more nickel to precipitate. An oxalate solution is useless for plating, because a nickel anode does not corrode to any extent in it. As nickel cannot be precipitated at all from a solution containing more than the merest excess of cyanide, the cyanide solution is not used as a plating bath. Plating could probably be carried on in a phosphate bath, but it is not known that there would be any advantage over a sulphate bath.

The plating baths for tin consist of an alkaline stannate solution and a so-called pyrophosphate solution. Since sodium pyrophosphate changes gradually in solution to disodium phosphate, it seems doubtful whether the advantages claimed for a "pyrophosphate" bath are really due to sodium pyrophosphate. Until this question is settled experimentally, it seems wiser not to consider this solution. Tin is determined analytically in ammonium oxalate solution and in ammonium

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[1] Die Galvanoplastik, 42.

[2] Cf. Brass World, 1906, 317.

[3] This state of things is gradually changing. Cf. Calhane and Gammage: Jour. Am. Chem. Soc., 29, 1268 (1907).

sulphide solution. There is no apparent reason why an acidified ammonium oxalate solution should not be used for plating purposes.[1] With regard to the sulphide solutions, the same question arises as with the sodium gold sulphide solution. No method is given in Smith's "Electro-Analysis" for the determination of tin in alkaline solutions, but I see no reason why such a method should not be worked out if anybody cared to experiment with it.

Plating baths for zinc consist of sulphate, cyanide, zincate, and chloride plus ammonium chloride. The sulphate and the chloride solutions yield a more coarsely crystalline deposit than do the zincate and cyanide solutions. As zinc is deposited rather as a protective covering than as a thing of beauty, a coarseness of crystalline structure is not a serious drawback though it unquestionably is not an advantage. Zinc is determined electrolytically in sulphate, acetate, citrate, cyanide, zincate and oxalate solutions. The zincate, sulphate, and cyanide solutions occur in both sets, the ammonium acetate solution is valuable only because of the solution not becoming strongly acid, and an acidified oxalate solution could undoubtedly be used as a plating bath.

The chloride-plating bath does not find its analogue among the analytical solutions and that brings us to what is for the moment a fundamental difference between the two kinds of solutions. Plating baths often contain chlorides; solutions for electrolytic analysis practically never did until recently. When a soluble anode is used, as in plating, there is no danger of free chlorine. With a platinum anode there is always danger of the solution containing free chlorine, hypochlorous acid, or hypochlorites, any one of which would cause trouble at the cathode. There is also a possibility of the platinum anode being attacked if the current density is high.[2] Except perhaps in the case of copper the objection is not to chlorides in themselves but to their decomposition products. If one were to add something to the solution, which would act

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[1] Cf. Curry: Jour. Phys. Chem., 10, 489 (1906).

[2] E. F. Smith: "Electro-Analysis," 4th Edition, 89.

as a depolarizer for chlorine and prevent its being set free, the disturbing effect would be eliminated. This has been done at the University of Pennsylvania in a very ingenious manner. A layer of toluene or xylene is placed above the solution and absorbs the halogen completely.[1] The general principle has been applied in an even more ingenious way in special cases,[1] also at the University of Pennsylvania. By using a silver anode the halogen is changed to the corresponding silver halide and can be weighed directly. This method of eliminating a difficulty gives a quantitative electrolytic determination of the halogens.

The general results of this paper may be summed up as follows:

(1) Cyanide and sulphate baths are used both for electroplating with copper and for the electrolytic determination of copper. The acid ammonium oxalate and acid phosphate baths are used only for the electrolytic determination of copper but could be used as plating solutions. That the cyanide solution can be used for the electrolytic determination of copper is made possible by the electrolytic oxidation of the cyanide at the platinum anode.

(2) Cyanide baths are used both for electroplating with silver and for the electrolytic determination of silver. A nitrate solution is used for the electrolytic determination only, since the deposited silver is too coarsely crystalline for plating purposes unless a very high current be used or a colloid be added.

(3) Cyanide and sulphocyanate are used both for electroplating with gold and for the electrolytic determination of gold. Ferrocyanide solutions are used as plating baths, but present no advantage over the cyanide and sulphocyanate from an analytical point of view, and therefore have not been studied with this in mind. Sodium gold sulphide solutions are used for electrolytic determinations, but the possibility of their forming a sulphide film of baser metal seems to make them objectionable for plating baths.

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[1] E. F. Smith: "Electro-Analysis," 4th Edition, 285.

(4) Nickel can be determined electrolytically in an ammoniacal sulphate solution, an ammonium oxalate solution, a cyanide solution, or an ammoniacal phosphate solution. Only a sulphate solution is used for plating. An oxalate solution would not corrode the anode while a cyanide solution would be too difficult to regulate. A phosphate solution could probably be used for plating.

(5) There is no relation between the plating and the analytical solutions with tin, plating being done with an alkaline stannate solution while ammonium oxalate and ammonium sulphide solutions are used for electrolytic analysis. It is possible that plating could be done with an oxalate solution and that tin could be determined analytically in an alkaline solution.

(6) Cyanide, sulphate, zincate, and chloride solutions are used in plating with zinc. The first three are also used for electrolytic analysis. Zinc is also determined electrolytically in an oxalate solution, which would probably work well as a plating bath.

(7) Chlorides are not permissible in solutions for analysis on account of the danger from chlorine, hypochlorous acid or hypochlorites. If a depolarizer for chlorine, like toluene, xylene or silver, is used the difficulties disappear except perhaps in some determinations of copper.

(8) A great deal more experimental work needs to be done before we understand all the problems connected with electroplating and electrolytic analysis, but the general principles seem to be fairly well established.

Cornell University

NEW BOOKS

Electro-Analysis. *By Edgar F. Smith. Fourth edition, revised and enlarged. 13 × 19 cm; pp. vi + 336. Philadelphia: P. Blakiston's Son and Co., 1907. Price: $2.50 net.*—With the publication of this volume we begin a new period in electrolytic analysis. While the old methods of determining metals electrolytically are still given for the benefit of those who may care to use them, the important things in the book are the new methods of rapid analysis which have been worked out at the University of Pennsylvania. The change in the time of a determination from hours to minutes is an astounding one. While the same preliminary results were obtained simultaneously and independently at Yale by rotating the cathode, and at the University of Pennsylvania by rotating the anode, the further development of the methods has been the work of Dr. Smith and his students. Nor has the use of the rotating anode been the only improvement.

By using a silver anode, chlorides, bromides, iodides, sulphocyanates, ferrocyanides, ferricyanides, phosphates and carbonates may be determined directly, while the resulting base may be titrated in the solution. This process can be improved upon by using a mercury diaphragm as in the Castner cell, collecting the alkali in the other compartment. It was then found that sodium, potassium, barium, and strontium passed readily through the mercury diaphragm while magnesium amalgam is decomposed in the inner or anode compartment, owing to the insolubility of the hydroxide. While calcium can be carried through to the outer compartment, this is not the case when magnesium is present and when the voltage is kept low enough. This discovery led to a method of separating sodium, potassium, strontium or barium from magnesium alone or from a mixture of magnesium and calcium. In the same way sodium, potassium, strontium or barium may be separated from iron, uranium, or aluminum. It is also possible to separate barium from cerium, lanthanum, neodymium, thorium and titanium. There seems to be no reason why this method should not be carried further. We know that the presence of nickel in mercury causes sodium amalgam to break up very rapidly. If it should prove not to work the same way with barium amalgam, a separation of sodium from barium would then be possible. It is quite conceivable that a catalytic agent could be found such that one could separate sodium from potassium. A study of the effects due to changing temperature might also be very profitable.

By using a cadmium anode, sulphides are determined directly, and fluorides can be analyzed by coating the anode with calcium hydroxide. While the most striking use of the mercury cathode is as a diaphragm in the determination of the alkalies and the alkaline earths, the use of the straight mercury cathode makes it possible to determine such metals as zinc more rapidly and more conveniently than ever before.

It is to Dr. Smith that we also owe the elimination of the bugbear in regard to chlorides in analytical determinations. By the addition of a layer of toluene or xylene, the difficulties attendant on the use of chlorides disappear because the chlorine reacts at once with the hydrocarbon.

It should now be clear that this book supersedes all previous ones on electrolytic analysis and that the methods now at our disposal are incomparably superior to those that we possessed seven years ago.

There is one point about the theory of the rotating anode which the reviewer would have liked to have seen stated more explicitly. Objection has been made in Germany to the method on the ground that the high voltage made a separation of metals impossible. The fact of such separations as that of copper from cadmium, p. 187, shows that this objection is not well founded; but it would have helped the student to have pointed out that the drop of potential through the solution accounts for most of the voltage and that the question of voltage does not come in anyway in the case of a constant current separation. These two points are touched upon in the introduction, pp. 39 and 52; but only as quotations from others and the reviewer knows from personal experience that this matter of the high voltage has proved puzzling to various people.

Wilder D. Bancroft

Abhandlungen ueber Elektrizität und Licht. *By Theodor von Grotthus. Ostwald's Klassiker der exakten Wissenschaften, No. 152. Herausgegeben von R. Luther und A. v. Oettingen. 12 × 19 cm; pp. 198. Leipzig: Wilhelm Engelmann, 1906. Price: bound, 3.00 marks.*—The first paper in the volume is the famous one on the theory of electrolytic conduction. In these modern days when a short paper is often classified as a "minor contribution" it is interesting to see that a short note of scant twelve small pages contains a theory which held the field for eighty years and which was superseded only when people changed from qualitative to quantitative measurements.

In the second paper we find Grotthuss studying the effect of a current upon sprouting seeds. His experiments seem to show the toxic action of the current, but it may be questioned whether the results were not really due to the seeds being in contact with the electrodes. It is quite likely that Grotthuss was really studying the toxic action of certain salts rather than the toxic action of the currents.

The papers on the chemical and electrochemical action of light have not received the same recognition as did that on the theory of electrolysis, but they are quite as important in their way. As far back as 1819 Grotthuss formulated definitely the law that only those rays of light, which are absorbed, can act chemically. This law is usually attributed to Herschel or to Draper which is the more remarkable because in 1853 Slater refers to the work of Grotthus. The views of Grotthuss on the electrochemical action of light have not yet become a part of our scientific knowledge, though they certainly are the closest approximation to truth that we have.

Wilder D. Bancroft

DECOMPOSITION CURVES OF LITHIUM CHLORIDE IN PYRIDINE AND IN ACETONE—THE EFFECT OF WATER

BY HARRISON EASTMAN PATTEN AND WILLIAM ROY MOTT[1]

Introduction

Lithium chloride is soluble in a number of organic liquids, and thus affords ready means for studying the effect of change in solvent upon the process of electrolysis. In the deposition of lithium from its chloride in a series of alcohols[2] we have considered only a simple solvent. This paper takes account of the influence of moisture on the electrolysis of lithium chloride in pyridine and in acetone, starting with the anhydrous solvents.

Part I. Electrolysis of Lithium Chloride in Pyridine

During the electrolysis of a pyridine solution of lithium chloride in an open cell,[3] there is a marked increase in the cell resistance. Thus, in a series of decomposition-curve determinations, polarization values for the total cell ranged from 4.00 volts[4] to 2.70 volts, and in some instances a rise of ten to a hundred fold was observed in the cell resistance. A preliminary attempt to take anode and cathode curves gave a polarization of 1.6 volts at the anode, and +0.4 volt at the cathode. As these solutions were not strictly anhydrous, it seemed advisable to study the effect of water. So several solutions were made up with great care to exclude moisture,

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[1] This work was carried out in the laboratories of physical chemistry and of applied electrochemistry at the University of Wisconsin, and the authors wish to express their appreciation of the courtesy extended to them by Professor L. Kahlenberg and by Professor C. F. Burgess.

[2] Jour. Phys. Chem., 8, 153 (1904).

[3] Compare, L. Kahlenberg: Jour. Phys. Chem., 3, 602 (1899); also, Laszczynski and Gorski: Zeit. Elektrochemie, 4, 290 (1897).

[4] These decomposition points were determined by extending back the CR line to the axis of the volts, thus subtracting the electromotive force used in overcoming the resistance of the electrolyte from the total electromotive force applied at the cell terminals.

and current electromotive force curves determined in dry cells. Anode and cathode curves were taken, using the potentiometer apparatus described in a previous paper.[1] Then water, in known amounts, was added and the curve redetermined. As a check on the conductivity of the solution, the specific conductivity of lithium chloride in pyridine at various dilutions was determined; and to ascertain how the added water changed the conductivity, a second conductivity curve was secured, showing the rapid increase in specific conductivity for small increments of water. With these data in hand, we can show that anhydrous pyridine containing anhydrous lithium chloride may be electrolyzed in a regular manner—an experimental fact—and that an extremely small quantity (about one-tenth percent) of moisture will cause the solution to act upon the lithium with the formation of an insulating film upon the *cathode*[2] of sufficient resistance to interrupt electrolysis.

Materials

A sample of pyridine from Kahlbaum was dehydrated over solid caustic potash, distilled and used at once. Its boiling-point was 114–117° C under 729.3 mm.

The lithium chloride was made by E. de Haën; after heating nearly to fusion for some time, a portion was quickly placed in a dry, weighed flask, stoppered, and weighed. Sufficient pyridine was run in just to dissolve the lithium chloride and the weight again taken. The solution contained 1.353 percent of lithium chloride on the total weight of solution; it is by no means a saturated solution, although it is very nearly one-third normal. Its specific conductivity at 25.0° C was 1.092×10^{-4} reciprocal ohms. Other solu-

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[1] Decomposition curves of lithium chloride in alcohols and the electrodeposition of lithium. Jour. Phys. Chem., 8, 153 (1904).

[2] Cathode films of great resistance are less common than the anode insulating films which have been observed by various experimenters with aluminum, magnesium, chromium, copper, lead, silver, etc. Consult further Electrochemical Industry, 2, 129, 268, 352, 444 (1904); Jour Phys. Chem., 8, 548 (1904).

tions from the same stock supply were made up as required. Where data is given, the solution used will be described.

Method

The decomposition curves were determined as described in a previous paper.[1] The impressed voltage, where small, was read on a potentiometer by compensation, and the small currents were measured by taking the fall of potential across a known resistance in series with the cell. Higher values were given by the carefully calibrated voltmeter and ammeter. The D'Arsonval galvanometer mentioned elsewhere,[2] served as a zero instrument. The electrolytic cell[2] was of glass with parallel fused-in platinum electrodes, three square centimeters in area and approximately 7 mm apart; its capacity was approximately 25 cc. A ground-in-glass stopper served to exclude moisture. Temperature was controlled by a water bath. Anode and cathode curves were taken by means of an Ostwald half cell, using an intermediate vessel containing lithium chloride dissolved in pyridine. The conductivity measurements were made by the Kohlrausch method, using a slide-wire bridge and telephone.

Results

First, experiments are given showing the effect on the decomposition curves of successive additions of water; then the total polarization, anode polarization and cathode polarization for a highly anhydrous solution; and finally the specific conductivity of solutions of lithium chloride in pyridine, mingled with varying amounts of water.

Table I contains in the first three columns the decomposition curve of the one-third normal solution of lithium chloride in pyridine, described under the heading "Materials." The current given in column II is the more exact—it was read on the potentiometer as voltage drop across a known resistance and calculated—while that in column III was

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[1] Jour. Phys. Chem., 8, 153 (1904).

[2] Potentials of zinc in aqueous solutions. Trans. Am. Electrochem. Soc., 3, 318 (1903).

taken on the milliammeter. The graph of this curve is not given, since a similar curve with anode and cathode values is to be presented below.

TABLE I

Electrolysis of one-third normal LiCl in pyridine, $t = 25°$ C

I Volts	II Amperes	III Amperes	IV Volts	V Amperes	VI Amperes
0.97	0.000031	—	—	—	—
1.33	0.000173	—	—	—	—
1.62	0.000384	—	—	—	—
1.89	0.000610	—	—	—	—
2.17	0.000835	—	—	—	—
3.36	0.00141	0.002	2.46	0.000394	—
3.90	0.00106	0.002	2.94	0.000551	—
4.44	0.00059	0.001	3.45	0.000482	—
4.89	0.00106	0.0015	3.96	0.000394	—
5.34	0.00157	—	4.45	0.000551	0.001
5.78	0.00216	0.0025	4.91	0.000945	0.0015
6.27	0.00264	0.003	5.37	0.001337	0.002
6.68	0.00320	0.004	5.82	0.001848	0.0025
7.58	0.00425	0.0045	6.25	0.002509	0.003
8.47	0.00531	0.006	6.71	0.00295	0.0035
9.35	0.00650	0.007	7.59	0.00409	0.004
10.24	0.00764	0.008	8.47	0.00531	0.006
11.13	0.00866	0.009	9.35	0.00649	0.007
12.04	0.00965	0.010	10.25	0.00748	0.008
12.94	0.01060	0.011	11.16	0.00843	—
13.84	0.01164	0.012	12.04	0.00965	0.010
9.40	0.0060	0.006	12.92	0.01082	0.011
7.64	0.00362	0.004	13.81	0.01195	0.012
5.83	0.00170	0.002			
3.99	0.00008	0.000			

Battery point 3.95 volts

Lithium deposited.

Then 0.031 cc distilled water was added and electrolysis continued 20 minutes with 0.0006 ampere per sq. cm before taking the following curve.

Several discharge potentials for *the total cell* were then taken.

Volts

2.70
3.0 to 3.5
3.0
2.80
3.95
4.10

TABLE I (*Continued*)

To the last solution 1 cc distilled water was added. The lithium adhering to the cathode was vigorously attacked. The solution was very nearly colorless. The following readings were then taken

VII Volts	VIII Ampere	IX Ampere
0.94	0.00059	—
1.40	0.00098	0.001
1.91	0.00090	0.001
2.36	0.00138	0.002
2.82	0.00177	—
3.35	0.00146	0.002
3.82	0.00177	0.002
4.32	0.00185	0.002
4.79	0.00208	0.002
5.28	0.00216	—
5.75	0.00252	0.003
6.24	0.00261	0.003
6.74	0.00261	0.003
7.69	0.00306	0.004
8.65	0.00354	—
9.63	0.00373	—
10.63	0.00373	0.005
11.61	0.00394	—
12.58	0.00421	—
13.55	0.00453	—
14.55	0.00453	0.006

After electrolyzing at 15 volts for a long while

1.78	0.000216
3.94	0.00059
5.93	0.00067
7.91	0.000945
9.88	0.00118
14.82	0.00177

After one hour of electrolysis

9.99	0.001455

Then the current was reversed and gave	
Volts	Ampere
10.00	0.011
8.00	0.011
6.00	0.006

After allowing the film to form on the new cathode, 10.78 volts passed only 0.00216 amperes through the cell.

It will be seen that this curve gives a decomposition voltage of 4.00 volts and that a discharge of 3.95 volts was obtained for the total cell. The deposit of lithium was smooth and had very little if any action upon the pyridine. Columns IV, V and VI show the curve for the same solution after adding 0.03 cc (0.12 percent) of distilled water, and electrolyzing with two volts pressure for twenty minutes. The presence of water makes it necessary to read the discharge voltages more quickly than in the previous case. A discharge of 4.1 volts was obtained after electrolyzing with a current density of 0.004 ampere per square centimeter for some time, showing that metallic lithium was deposited. However, a graph of this second curve shows the gradual increase in resistance of the cell as the water assists in the formation of an insulating film at the cathode. This film is yellow-red, and the solution, too, takes on this color. The anhydrous solution electrolyzes with but slight change in color.

Columns VII, VIII and IX give the effect upon the same solution produced by adding 1 cc of distilled water. The original volume of the solution was 25 cc. The resistance of the cell has increased considerably, owing to the formation of this cathode insulating film. On reversing the current, the film separates and strips from the electrode, and the normal resistance of the cell obtains until the lithium which is deposited on the new cathode again reacts to form the insulating film, and then the resistance rapidly rises.

Solutions of lithium chloride in pyridine were electrolyzed to the extent of eighteen different solutions and accurate readings of the impressed electromotive force and the current taken. Solutions of lithium chloride in pyridine containing less than 1 percent water have been electrolyzed with the formation of cathode insulating films having critical voltages of 40 and 60 volts. By critical voltage[1] is meant that voltage at which the film breaks down and allows accelerating amounts

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[1] Compare "Electrical Properties of the Films that form on Aluminum Anodes," Electrochem. Ind., September, 1904.

of current to pass. The rate of formation of the insulating film is much slower than with aluminum anodes, but in some cases the insulation here reaches 100,000 ohms per square centimeter. This resistance was sufficient to make the cell resistance appear greater for the solution than for the pure solvent.

In Table II, the voltage-current curve is given for a pyridine solution containing approximately 1 percent of water. The solution had been electrolyzed for a few hours before these readings were taken, and the low current passing shows the typical behavior of insulating films.

TABLE II

Electrolysis of a solution of lithium chloride in pyridine (one-third normal) containing 1 percent of water

Volts	Ampere
10	0.000020
20	0.000024
30	0.000070
40	0.000102
50	0.000196
60	0.003
70	0.040
80	0.120
90	0.300

Table III gives the complete data for a typical anhydrous solution of lithium chloride in pyridine. Column I contains the total voltage impressed on the cell; column II, the anode polarization; and column III, the cathode polarization. The current and current density (amperes per square centimeter) are found in columns IV and V respectively.

Lithium was deposited and no insulating film appeared on the cathode for twenty minutes. Then a yellowish-red film formed and the resistance rose. At first this solution was highly anhydrous, but some moisture from the air and from the intermediate cell which connected with an Ostwald half cell diffused down the neck of the electrolytic cell until finally the lithium was attacked. Thus this last experiment shows

TABLE III

Current electromotive force curve for lithium chloride dissolved in pyridine, one-third normal. $t = 24.8°$ C

Volts			Ampere	
I Total	II Anode	III Cathode	IV Current	V Current density per sq. cm
0.00	—0.59	—0.59	0.000000	0.000000
1.00	—1.15	—0.17	0.000039	0.000013
1.49	—1.43	+0.07	0.000118	0.000039
1.98	—1.43	+0.54	0.000157	0.000052
2.47	—1.43	+0.94	0.000200	0.000067
3.29	—1.47	+1.76	0.000208	0.000069
3.59	—1.51	+2.27	0.000413	0.000138
4.07	—1.51	+2.54	0.000432	0.000144
4.37	—1.58	+2.75	0.000630	0.00021
4.46	—1.68	+2.84	0.00104	0.00035
4.61	—1.76	+2.90	0.00139	0.00046
4.99	—1.90	+3.06	0.00201	0.00067
6.30	—3.04	+3.24	0.007	0.0023
7.31	—3.31	—	0.00869	0.0029
8.19	—3.51	—	0.00807	0.0027
9.09	—3.82	—	0.00906	0.0030

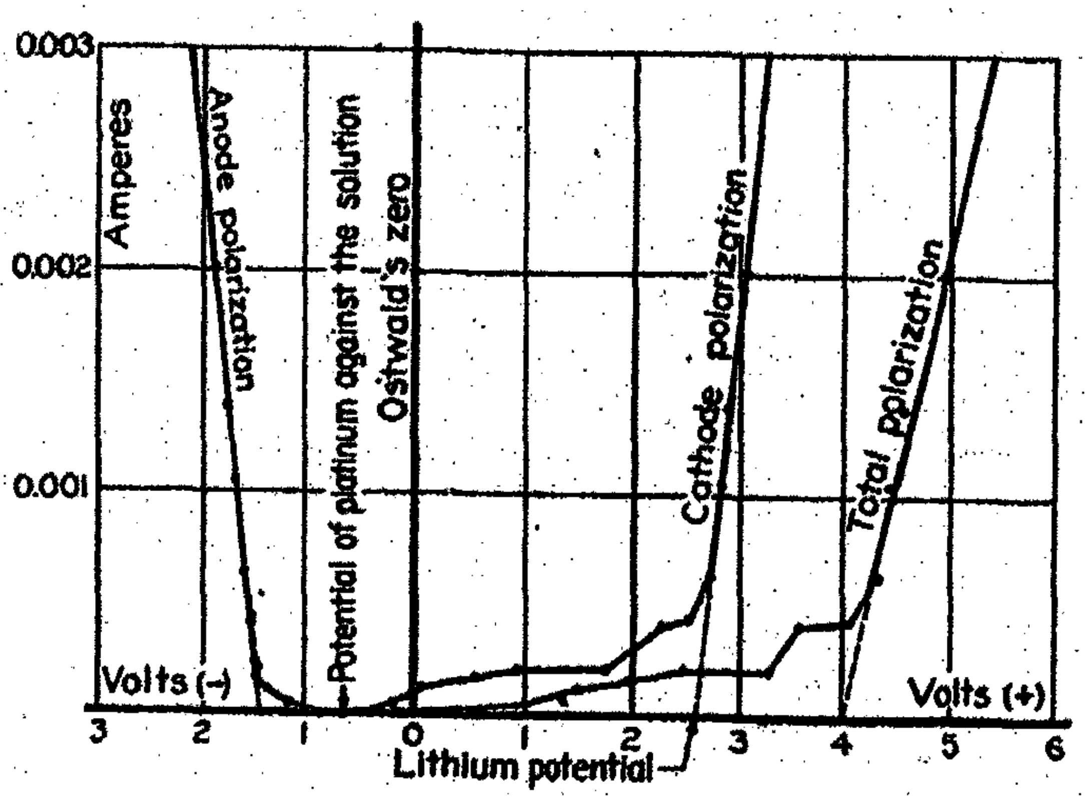

Fig. 1—Lithium chloride dissolved in pyridine

excellently the transition from anhydrous to very slightly hydrated solution. Fig. 1 represents Table III graphically.[1]

Ordinates are in amperes, abscissas in volts—positive to the right of the reference zero, negative to the left. The anode and cathode curves rise from the common point —0.59 volt, which represents the experimental result of measuring the potential of the platinum[2] electrodes against the solution of lithium chloride in pyridine. This is comparable to the rise of anode and cathode curves from the common potential of —0.8 volt, using lithium chloride in water between platinum electrodes. This common point represents a finite value of anode and cathode polarization for zero current. As our reference zero we have used —0.56 volt for Ostwald's normal half cell. This zero is called for convenience "Ostwald's zero." Any other zero might have been used without affecting any of our results or conclusions.[3]

Fig. 1 shows that at the current density of 0.001 ampere per square centimeter, the cathode polarization is +2.60 volts, the anode —1.40, and the total 4.00 volts. The chemical reactions that determine these polarizations are briefly as follows:

At the cathode, three sets of reactions occur with increasing current density. At very low current density, the

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[1] The diagrams and description given in the Journal of Physical Chemistry, 8, 163 (1904), under the head "Decomposition Curves of Lithium Chloride in Various Alcohols, Etc.," will aid materially in getting a clear understanding of this set of curves See also "An Analytical Study of the Deposition of Aluminum from Ethyl Bromide Solution," Jour. Phys. Chem., 8, 557 (1904).

[2] This is merely the usual mode of speaking. It is conceded that platinum does not enter into reaction with the electrolyte. The source of the potential difference is considered to be in the reactions of the oxygen dissolved in the electrolyte and in the platinum. Glaser's (see Zeit. Elektrochemie, 4, 373) tests on the oxyhydrogen cell, using the solvents alcohol, ether, acetone, etc., are of interest in discussing the potential differences of dissolved gases. But it must be borne in mind that Kelvin's work on contact electromotive force shows that an electrolyte is not needed to produce a difference of potential between substances. In the present instance we have the potential of the dissolved gas predominating.

[3] At present the selection of a reference zero is entirely on an arbitrary basis. See the work of Carveth, Nernst, Ostwald, Billitzer and Palmaer.

oxygen at the cathode acts as a nearly perfect depolarizer, and no hydrogen or other products appear. At higher current densities, if the electrolyte contains minute quantities of water, then reaction takes place at +0.4 volt, giving off hydrogen or other gas and forming lithium hydroxide; at a comparatively low current density of 0.001 ampere per square centimeter metallic lithium separates from solution in mass and establishes its counter-electromotive force. The energy of the reaction of the primary product on the solvent is returned to the circuit as long as the current density does not exceed the rate of action of the solvent on the metallic lithium. But massive lithium once plated out, redissolves,[1] evolving heat and not returning electrical energy to the circuit. That is, the true single potential of metallic lithium is obtained on its first appearance in mass. This potential is +2.60 volts, which value is higher than that calculated for aqueous solution as +2.45 volts and observed with alcohol solution as +2.41 volts. The high single potential of lithium experimentally found with pyridine as solvent is indicated by the high heat of solution of lithium chloride in pyridine. The heat of solution of 4.06 percent lithium chloride in pyridine at 16° C was found to be 13,920 calories, which gives 0.613 volt.[2] Similarly for an aqueous solution the heat of solution in volts is 0.371 volt. The difference, 0.242 volt, is of the same order of magnitude as the difference (+0.15 volt) between the cathode voltage determined experimentally and that calculated from thermal data; similarly this difference is +0.19 volt, when we compare the cathode voltage in pyridine solution with that for alcoholic lithium chloride solution—where the heat of solution is not at hand.[3] Thus

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[1] Compare the rate of action of the solution at different current densities for amyl alcohol solution of lithium chloride. Jour. Phys. Chem., 8, 181 (1904).

[2] $\frac{13{,}920 \times 4.24}{96{,}540} = 0.613$ volt

[3] Compare with this the correspondence between the heat of solution of aluminum bromide in ethyl bromide, and the decomposition point of the solution, 2.30 volts, as shown in former papers. Jour. Phys. Chem., 8, 548 (1904); "On the Heat of Solution of Aluminum Bromide in Ethyl Bromide," Trans. Am. Electrochem. Soc., 7, 177 (1905).

we have confirmed the first part of the work of Laszczynski and Gorski, that pyridine unites with lithium chloride, evolving much heat,[1] but we made no attempt to reproduce the crystalline body which they describe, $LiCl + 2C_5H_5N$.

At the anode, the polarization —1.40 volt is observed at a current density of 0.00003 ampere. This polarization is 0.30 volt less than for alcoholic solutions. For dilute aqueous solution the voltage at which free chlorine separates has been calculated[2] as —2.00 volts. In alcoholic solutions the chlorine apparently replaces the hydrogen of the hydrocarbon group, also gives alkylchlorides, and forms free hydrochloric acid at the anode.

Anderson[3] has shown that chlorine, bromine and iodine do not replace hydrogen on the pyridine ring at ordinary temperatures, but rather form unstable addition products. The low polarization at the anode found when chlorides are electrolyzed in pyridine accords with such reactions. When zinc chloride is used as solute, the same low anode value is obtained for a low current density. But at 0.020 ampere per square centimeter of anode surface this zinc chloride solution in pyridine shows the same higher value of anode polarization which characterizes the electrolysis of chlorides in alcohols, for a considerable range of current density. The reason for this is, possibly, that with greater electrical energy available the liberated chlorine substitutes one or more hydrogens on the pyridine ring, as would happen if the chlorine were acting upon pyridine at a higher temperature.[4]

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[1] Bonnefoi, Comptes rendus, 129, 1257 (1899), has determined the heat evolved when LiCl unites with 1, 2 and 3 molecules of ethylamine; these values are respectively 13,834, 11,517 and 10,570 small calories, and agree well with the values calculated from the temperature of dissociation by means of Clapeyron's formula.

[2] "Experimental Determinations of the Single Potentials of the Alkali Metals, Sodium and Potassium," Electrochem. Ind., September, 1903. Also "Single Potentials of the Halogen Elements," Trans. Am. Electrochem. Soc., 5, 73 (1904).

[3] Trans. Roy. Soc., Edinburgh, 21, 4, 571; also Annalen, 105, 340.

[4] Compare "The Behavior of Pyridine Dissolved in Acetic Acid," Jour. Phys. Chem., 6, 554 (1902).

The influence of water upon the specific conductivity of pyridine alone is interesting. The pyridine used showed a resistance of 625,000 ohms per cubic centimeter, corresponding to a specific conductivity of 1.61 × 10^{-6}. When 7.30 cc of this pyridine were diluted with 0.031 cc of distilled water, the conductivity rose to 4.00 × 10^{-6}, and when a second portion of water, 0.031 cc, was added, the specific conductivity was 10.42 × 10^{-6}, an increase of nearly 900 percent for an addition of 0.85 percent of water. Laszczynski and Gorski appear to have used pyridine with a specific resistance of only 100,000 ohms per cubic centimeter. They failed to pass the direct electric current through concentrated solutions of several salts in this pyridine, and it is possible that by use of drier pyridine—and consequent lack of film formation at electrodes—some of these solutions might show appreciable conductivity.

Table IV below contains values for the specific conductivity of lithium chloride in pyridine at nine dilutions.

TABLE IV

Specific conductivity of lithium chloride in pyridine at 25° C

Percent of lithium chloride	Specific conductivity × 10^{+4}
0.052	0.171
0.064	0.187
0.092	0.211
0.57	0.723
0.62	0.741
0.71	0.773
0.83	0.800
0.99	0.889
1.35	0.953

The effect of lithium chloride upon the conductivity of pyridine is much greater than that of water, for the first portion added, but the increase in conductivity produced by succeeding portions of salt is relatively less than where water alone is added to dry pyridine drop by drop.

Table V shows the effect of water upon the specific conductivity of a one-third normal solution of lithium chloride in pyridine.[1]

Table V

Effect of water on the conductivity of *n*/3 lithium chloride in pyridine

Water-parts by volume added to 100 of the solution	Specific conductivity $\times 10^{+4}$
0.00	1.092
0.22	1.303
0.55	2.14
0.72	2.54
1.17	4.90
1.49	5.21
1.93	5.75
3.10	7.33
3.53	8.06
3.97	8.56
4.42	9.20
4.85	9.90
5.28	10.43
12.7	17.24
19.7	19.20
48.0	23.30
76.0	26.40
160.0	27.00

An addition of 0.5 percent of water by volume doubles the conductivity of the one-third normal solution. This large increase in the specific conductivity on adding water would tend to facilitate electrolysis if the high resistance film were not also thereby developed on the cathode, prohibiting electrolysis. The other alkali metals, sodium and potassium, form dark brown coatings on standing in pyridine. They are readily melted in anhydrous pyridine. The formation of the red coat is accelerated by adding a drop of water to the pyridine. These films also form on the cathode when potassium iodide and salts of other alkali and alkaline earth metals are electrolyzed in pyridine solution.

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[1] Compare this with the effect of water upon the specific conductivity of a solution of pyridine, 17 percent; in acetic acid, 83 percent. Influence of the solvent in electrolytic conduction. Jour. Phys. Chem., 6, 554 (1902).

Current Efficiency

A rough determination of the current efficiency in depositing lithium from a saturated solution of lithium chloride in pyridine was made. The platinum wire cathode, 2.5 cm long, was placed under an inverted burette, which thus served to collect and measure the gas evolved. The anode was a sheet of platinum foil of 29.5 cm effective area. The cell was carefully sealed to prevent access of moisture, and lumps of solid fused lithium chloride in contact with the solution assisted in maintaining it in a dry condition.

The current gas evolved at cathode and the time are given in Table VI. Fig. 2 shows this same set of values graphically. Curve 1 represents the increase of cathode gas with time, ordinates (not corrected for t and p) being cubic

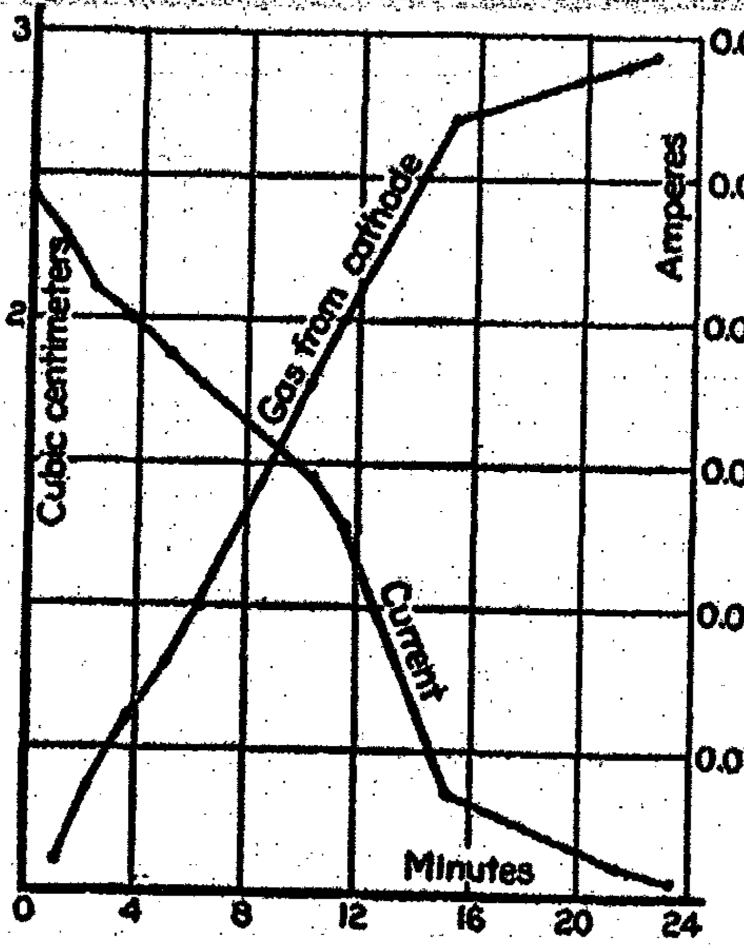

Fig. 2—Saturated solution of lithium chloride in pyridine. Temp. 18°; $p = 702.3$ mm (corrected). Current density 0.001 amp/sq cm

centimeters of gas, and abscissas time in minutes. Curve 2 is the decrease in current with time, the abscissas being exactly the same as for Curve 1; and the ordinates (given at the right hand), amperes. A comparison of these two curves

TABLE VI

Showing the decrease of current with time, and the parallel decrease of gas evolved at cathode, owing to film formation, the electromotive force on the cell remaining constant at 108 volts.

$t = 18°$ C

Time		Gas	Current
Minutes	Seconds	cc	Ampere
0	0	0.0	0.0485
1	10	0.1	0.046
1	40	0.2	0.045
2	15	0.36	0.042
2	55	0.4	—
3	30	0.55	—
3	45	0.60	0.040
4	40	0.74	0.038
5	10	0.8	0.0375
6	25	1.00	0.0355
10	25	1.75	0.029
11	30	2.00	0.0255
15	10	2.70	0.007
21	30	2.90	0.002
22	25	2.93[1]	0.001
34	30	3.06[2]	—
73	10	3.10	—
95	00	3.15[3]	—
281	00	—	—

shows that the cathode gas is evolved at a constant rate, regardless of the vagaries of the current passing through the cell, until the current has fallen to about one-seventh of its initial value. This steady evolution of gas is exactly what is to be expected if the lithium deposits as a primary decomposition product and subsequently acts upon the solution at a steady rate, decomposing the solution. The sudden drop in the rate of gas evolution after fifteen minutes of electrolysis is evidently due to the formation of a film upon the lithium. The resistance of this film to the passage of the

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[1] 2.93 cc = 2.53 cc at 0° C and 760 mm.

[2] No voltage on cell, gas still evolved.

[3] No further evolution of gas.

current seems not to prevent the action of the solution upon the deposited lithium, until a considerable thickness of film has been reached, since the current passing through the cell decreases from the very beginning, and its curve seems to indicate by its change of direction (see Curve 2, Fig. 2) two stages in the formation of the film.

It is interesting to note that this evolution of gas from the cathode was maintained long after the electromotive force had been taken off the cell, although the volume of gas was very small.

A graphical integration of the current-time Curve 2 in Fig. 2, shows that some 32.44 coulombs have passed through the cell. This is equivalent to 3.30 cc hydrogen at 0° and 760 mm. There was evolved in this experiment 2.53 cc gas (reduced to 0° and 760 mm) while the current was passing. Assuming that this gas was all hydrogen, 76.7 percent of the current was used for its production, and 23.3 percent for the deposition of lithium which remained unattacked by the solution. This calculation of course assumes that the total current is used, either in depositing lithium or in liberating gas. The area of the platinum cathode used here was about 0.5 cm, which gives an initial current density of 0.1 ampere per sq. cm, or some 90 amperes per sq. foot.

Upon reversing the current, lithium is deposited upon the new cathode, while the film upon the old cathode—now the anode—separates in a sheet and falls away. In a short time—some 10 to 15 minutes—a film again forms upon the cathode and the current rapidly falls to a negligible quantity. This film formation takes place more rapidly in a solution which has been electrolyzed than in a fresh solution, probably owing to anode products remaining near the electrode, which upon reversal of the current becomes the cathode.

Thus we have shown the conditions for the continuous deposition of metallic lithium from a solution of lithium chloride in pyridine to be: (1) A current density of 0.001 ampere per square centimeter of cathode surface, at 25° C; (2) The solution should be anhydrous to a high degree; (3)

The electromotive force necessary to produce the required current density will depend upon the specific resistance of the solution, upon the size of electrodes and their proximity to each other; and in addition it must overcome the cathode polarization—2.60 volts for this current density—and the anode polarization. This last will depend upon the area of the anode. When cathode and anode are alike in area, as in our experiments, the total polarization at 0.001 ampere per square centimeter is 4.00 volts, of which -1.40 volts is at the anode, and 2.60 volts at the cathode. But a smaller anode with the same cathode would show a higher polarization, and thus add to the total requisite impressed electromotive force. The current efficiency has been shown by a rough experiment to be some 23 percent for the deposition of lithium, using a current density of 0.1 ampere per sq. cm, but electrolysis was soon stopped by the formation of a film upon the cathode.

Part II. The Deposition of Lithium from Acetone Solution

Metallic lithium may be deposited from the solution of its chloride in acetone[1] at the low current density of one milliampere per square centimeter; or, roughly, about one ampere per square foot of cathode surface. The conditions requisite for this deposition and the phenomena attendant upon it have been considered experimentally. These comprise anode, cathode and total polarization as a function of the current density; the influence of secondary reaction at the electrodes upon the form of the current electromotive force curve; the effect of water—either present as impurity or produced by electrolysis—upon the conductivity of the solution, and its tendency to form a cathode film by further reaction; the relation of cathode material to the current density at which lithium deposits; and the current efficiency with which the lithium is deposited.

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[1] This was presented to the American Chemical Society at its summer meeting in 1903. Compare Siemens: Zeit. anorg. Chem., 41, 270 (1905); also Levi and Voghera: Gazz. chim., 35, 277 (1905).

Materials

The acetone was chemically pure from Kahlbaum and distilled at 54.7° C under a pressure of 739 mm. The lithium chloride was from E. de Haën.

Methods

The procedure followed in securing data on the total polarization, anode polarization and cathode polarization, as affected by current density, have been described in Part I of this paper together with the methods used to determine current efficiency and electrical conductivity (Kohlrausch).

Results

Table VII contains the current-voltage readings for a 0.94 percent solution of lithium chloride in acetone.[1] The electrolysis was carried out between platinum electrodes, 3 sq cm in area and approximately 7 mm apart. The cell was closed by a ground-in glass stopper, to exclude moisture.

The current electromotive force curve (Fig. 3) plotted from the data in Table VII shows a sudden rise in the counter-electromotive force at a current density of 0.001 ampere per square centimeter, from 2.1 volts to 4 volts for the total cell.

This same saturated solution of lithium chloride was electrolyzed for about an hour with an impressed electromotive force of 110 volts and an initial current of 1.0 ampere. The lithium was deposited in a spongy condition and consequently appeared black to gray, whereas the compact deposit of lithium from this solution is white, like a zinc deposit. The lithium was obtained in a deposit some 2 mm thick. When placed under benzene the metal reacts with the water in the benzene liberating hydrogen, and when this trace of water is exhausted the lithium keeps very well.

In order to locate more definitely this change in the polarization of the cell when lithium is deposited, the polarizations at anode and cathode, as well as the total polarization

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[1] Compare "On the Deposition of Zinc from Zinc Chloride Dissolved in Acetone," Jour. Phys. Chem., 8, 483 (1904).

TABLE VII

Decomposition curve for a saturated solution of lithium chloride in acetone (0.94 percent LiCl) at 21° C.

Volts	Ampere	Volts	Ampere
0.43	0.0000070	15.0	0.020
0.87	0.0000136	10.0	0.010
1.16	0.0000341	7.0	0.005
1.27	0.0000735	5.0	0.002
1.36	0.0001845	4.0	0.000
2.20	0.00080	—	—
2.83	0.00172	—	—
3.70	0.00300	—	—
4.74	0.00261	—	—
5.58	0.00422	—	—
6.38	0.00622	—	—
7.18	0.00825	—	—
7.97	0.01030	—	—
7.91	0.01084	—	—
7.16	0.00844	—	—
6.34	0.00663	—	—
5.58	0.00421	—	—
4.75	0.00249	—	—
3.97	0.00028	—	—

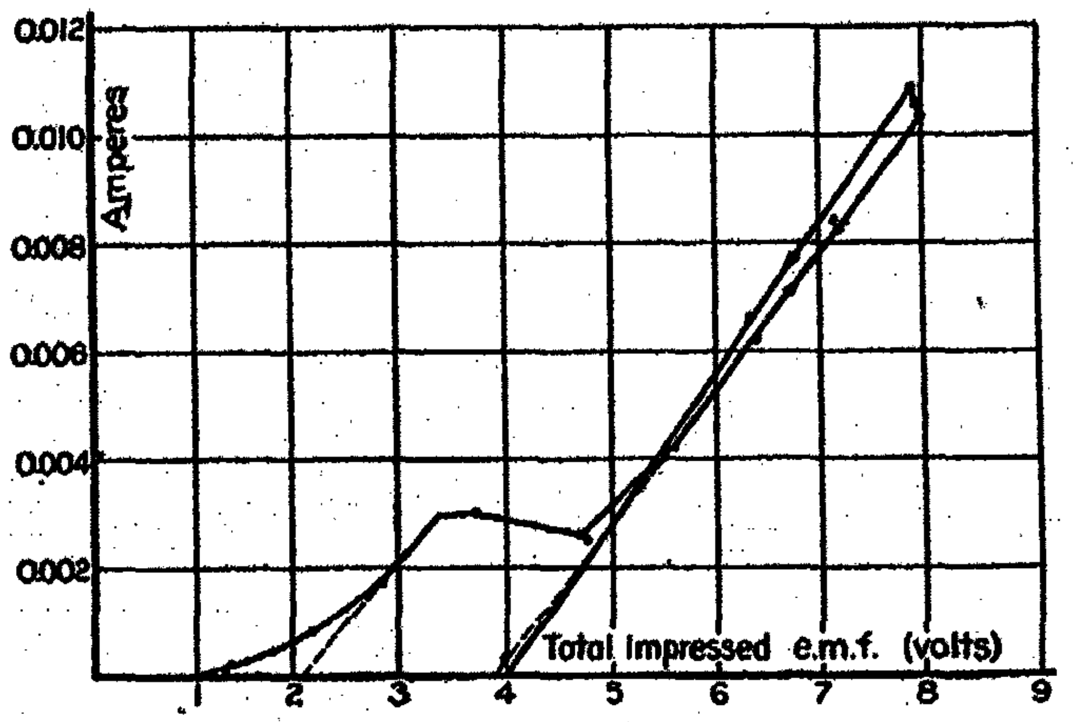

Fig. 3

of the cell, were taken at different current densities. These readings are given in Table VIII, and shown graphically in

Fig. 4. The electrical connections, instruments and adjustments have been described above in Part I of this paper, which deals with the deposition of lithium from lithium chloride dissolved in pyridine. The solution of lithium chloride in acetone, used for the determinations given in Table VIII, was made up from acetone which had stood for weeks over calcium chloride, and was freshly distilled. The lithium chloride was fused and while still hot added to the acetone. Inspection of the data in Table VIII shows a lack of agreement between the total electromotive force on the cell and the sum of anode and cathode voltages. This discrepancy is due to the high resistance in series with the half cell, which rendered impossible the readings of the electromotive force closer than hundredths of a volt with the zero instrument at hand.

TABLE VIII

Current electromotive force curves for lithium chloride dissolved in acetone, 0.94 percent LiCl. $t = 27.0°$ C.

Volts				Ampere
Total	Cathode	Anode	Anode + cathode	
0.92	—0.28	—1.19	0.91	0.000138
1.25	—0.09	—1.27	1.18	0.000237
1.52	+0.07	—1.39	1.46	0.000474
1.72	+0.15	—1.43	1.68	0.000732
1.84	+0.23	—1.59	1.82	0.00105
2.00	+0.34	—1.67	2.01	0.00140
2.13	+0.51	—1.75	2.26	0.00176
3.28	+1.42	—1.94	3.36	0.00385
3.73	+2.20	—1.44	3.66	0.00128
3.85	+2.28	—1.63	3.91	0.00059
4.34	+2.72	—1.55	4.27	0.00079
4.65	+2.80	—1.70	4.50	0.00172
4.91	+2.99	—2.02	5.01	0.00296
5.21	+3.11	—1.98	5.09	0.00395
5.79	—	—	—	0.00606
6.36	—	—	—	0.00820
7.05	—	—2.52	—	0.00902

In Fig. 4 the anode and cathode curves both start from the same point—0.731 volt—at zero current, since this is the single potential of the platinum electrodes in this solution. Consider first the anode curve (III): its slant shows a CR line with about half the total drop in voltage due to the total cell resistance; on extending back this CR line, it intersects the axis of volts at —1.60 volts, and this value subtracted from the total polarization of the cell, +4.15 volts, gives as the cathode polarization +2.55 volts.

The cathode curve starts at —0.731 volt, but as the oxygen dissolved in the platinum is exhausted and as the solution at the cathode increases in alkalinity, the polarization gradually approaches the value +0.5 volt, which likewise is the value given by hydrogen in aqueous alkaline solutions. This change is in progress along the portions of Curve II marked a_2 b_2. At the point b_2 a rapid rise in polarization takes place, due to the deposition of metallic lithium, and at c_2 the counter electromotive force of the lithium is made more strongly evident by causing a large decrease in the current passing through the cell. This effect is observed until the point d_2 is reached, and finally at e_2 the cathode current electromotive force curve (e_2 f_2) again becomes simply a straight CR line, indicating that the current passing through the cell is proportional to the applied electromotive force. Extending this line e_2 f_2 back to the axis of volts gives a cathode polarization of +2.60 volts.

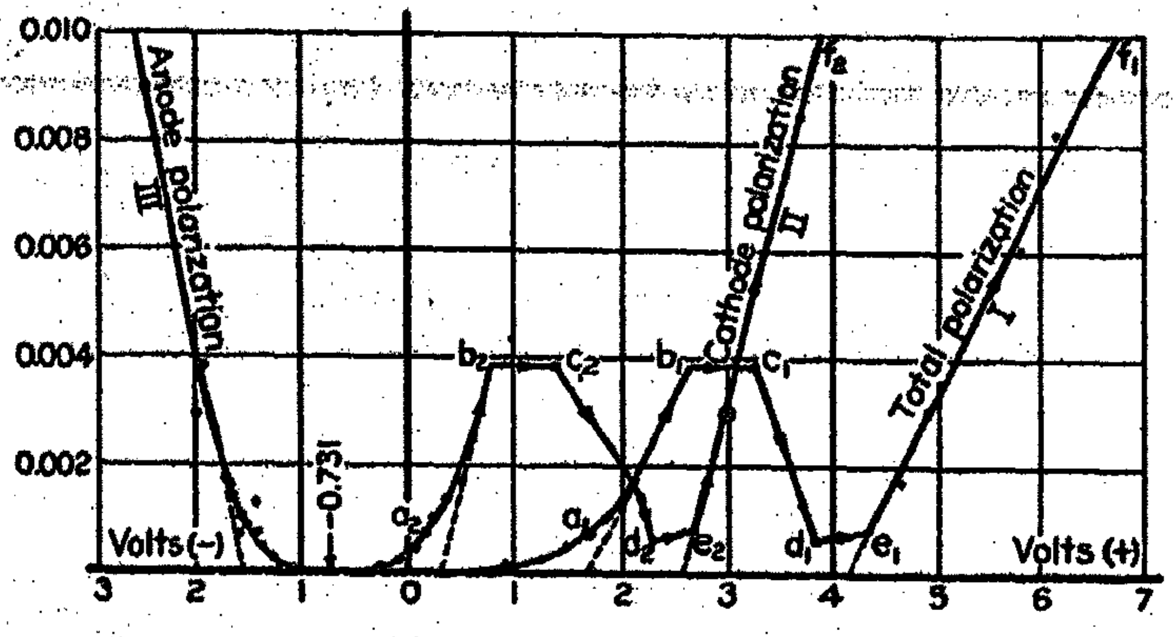

Fig. 4—Decomposition curves of lithium chloride in acetone

The "Total Polarization," Curve I, reproduces each change of curvature seen in Curve II for the cathode polarization. Since the platinum electrodes oppose each other, this total polarization curve starts from 0 volt at zero current; its rise along $a_1\,b_1$ expresses both the anode and cathode reactions, and at b_1 the same sudden rise in polarization is seen as at b_2 on the cathode curve. The CR line $e_1\,f_1$ has a steeper slant than the cathode CR line, $e_2\,f_2$, since the cathode CR drop is only about half that across the total cell. This same consideration applies to each of the branches of Curves I and II; thus $c_1\,d_1$ is steeper than $c_2\,d_2$, and $a_1\,b_1$ than $a_2\,b_2$.

The cathode polarization +2.60 volts given by the data in Table VIII is higher than that calculated for metallic lithium against aqueous solutions. The cathode discharge potential of lithium in this same solution of lithium in acetone was found to be +2.45, +2.53 and +2.45 volts, but when one drop of water was added to 25 cc of solution the discharge fell off to values intermediate between +2.45 volts and +0.46 volt.

The heat of solution of lithium chloride, 0.254 percent in acetone at 13° C, was found to be 5,883 small calories, which corresponds to 0.254 volt. The heat of solution of lithium chloride (4.06 percent) in pyridine, was found to be 13,920 small calories, which gives 0.613 volt.

The heat of solution of lithium chloride in water, which is equivalent to 0.371 volt, is 0.117 volt greater than for acetone solution, and 0.242 volt less than for pyridine solution. Since the acetone solution was very dilute (0.254 percent), the value found for the heat of solution is near the maximum.

The reaction of lithium upon the acetone itself is probably analogous to the action of sodium, which gives $CH_3.CO.Na.CH_2$ according to Freer.[1] The hydrogen thus liberated would again react with the acetone to give water and secondary alcohol and alcoholates as well as lithium

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[1] Am. Chem. Jour., 12, 355 (1890).

hydroxide; these products can react further to produce still higher alcohols and esters.

The effect of water upon the conductivity of an anhydrous solution of lithium chloride in acetone is given in Table IX, and the data plotted in Fig. 5. For the first portions of water added the conductivity increases regularly. This increase is much less than that produced by adding water to lithium chloride dissolved in pyridine, as shown in Part I of this paper. When some 0.6 percent of water (by volume) has been added to the acetone solution a precipitate begins to form and presently collects at the bottom of the conductivity cell as a second liquid phase. The platinized platinum electrodes were held vertically so that they remained in the acetone-lithium chloride phase throughout the experiment. The separation of this second liquid phase rich in lithium chloride and water is indicated by the drop in the electrical conductivity, which rose again on standing, since this second liquid layer dissolved in the main body of the solution as soon as the equilibrium, temporarily disturbed by addition of water, could readjust itself. On adding more water—0.824 percent in all—this effect was still more pronounced. A considerable volume of the second liquid phase formed and the

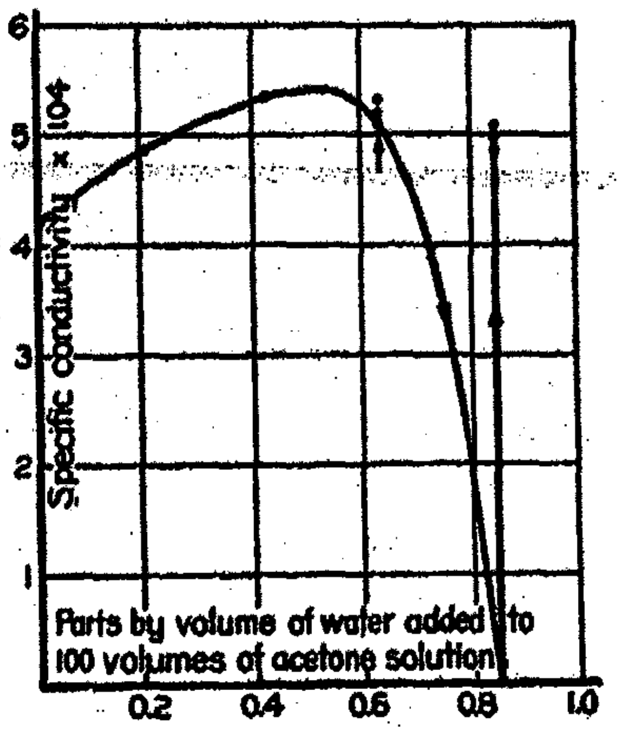

Fig. 5—Effect of water upon specific conductivity of lithium chloride acetone. Temp. 25.0°

conductivity dropped suddenly, as shown in Fig. 5, but on standing 75 minutes with occasional shaking the second liquid layer again went back into the solution and the conductivity rose to nearly the same final value as before, when 0.618 percent of water had been added.

Table IX

Effect of water upon the specific conductivity of anhydrous lithium chloride in acetone, 0.94 per cent. $t = 25.0°$ C.

Parts of water by volume added to 100 parts of the saturated acetone solution	Specific conductivity	Time	
		Minutes	Seconds
0.0	4.23×10^{-4}	—	—
0.206	4.87×10^{-4}	—	—
0.412	5.345×10^{-4}	—	—
0.618	5.11×10^{-4}	0	—
0.618	5.215×10^{-4}	45	30
0.618	5.285×10^{-4}	138	0
0.824	1.785×10^{-6}	0	—
0.824	1.785×10^{-6}	2	—
0.824	1.545×10^{-5}	4	30
0.824	4.87×10^{-4}	9	30[1]
0.824	4.89×10^{-4}	12	0[2]
0.824	4.97×10^{-4}	15	30[3]
0.824	5.095×10^{-4}	75	—

If water is formed at the cathode during the deposition of lithium it is evident that a second liquid phase may be formed and, temporarily at least, greatly increase the resistance. The stirring of electrolyte produced by the liberated hydrogen will tend to prevent this effect.

Current Efficiency

Using the same apparatus described in Part I of this paper, the current efficiency for the deposition of lithium chloride from an anhydrous saturated solution (0.94 percent) of lithium chloride in acetone was found to be 38.5 percent

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[1] After shaking.

[2] Not shaken.

[3] Shaken.

at a current density of 0.001 ampere per square centimeter, and at 20.5° C. This calculation assumes that the gas liberated at the cathode is hydrogen. Similar experiments using a saturated anhydrous solution of lithium chloride in amyl alcohol gave a current efficiency for the deposition of lithium of 44.8 percent with an average current density of 0.0012 ampere per square centimeter, at 22° C. For lower current density where no metallic lithium remained on the cathode, the volume of cathode gas liberated agreed within 1.2 percent with that required by Faraday's law, supposing the gas evolved to be hydrogen.

Summary

In this paper it has been shown that:

(1) Lithium may be deposited from an anhydrous saturated solution of lithium chloride in pyridine upon a smooth platinum cathode at a current density of 0.001 ampere per square centimeter, the temperature being 25° C.

(2) Lithium may be deposited from an anhydrous solution of its chloride in acetone under exactly the same conditions given in 1 above.

(3) The cathode polarization due to deposited lithium is +2.60 volt, both in the pyridine solution and in the acetone solution, despite the fact that in acetone the heat of solution was found to be equivalent to 0.254 volt and in pyridine to 0.613 volt—as compared to 0.371 volt in water.

(4) A very small quantity of water in the pyridine solution will cause the formation of an insulating film upon the cathode, and shortly stop the passage of the current.

(5) The specific electrical conductivity of lithium chloride in pyridine was measured at nine dilutions.

(6) The effect of water upon the electrical conductivity of solutions of lithium chloride in pyridine, as well as in acetone, was determined. The conductivity of the pyridine solution is raised in a high degree by a small percentage of water, while the acetone solution shows a much smaller rise on adding water, and may have its conductivity very greatly

lowered owing to the formation of two liquid phases, the water-rich phase having the higher percentage of lithium chloride.

(7) The current efficiency in depositing lithium from the pyridine solution was found to be 23.3 percent at a current density of 0.1 ampere per square centimeter; from acetone solution, 38.5 percent at a current density of 0.001 ampere per square centimeter; from amyl alcohol solution, 44.8 percent at a current density of 0.0012 ampere per square centimeter.

THE PROBLEM OF CHEMICAL AFFINITY[1]

BY WILDER D. BANCROFT

I. INTRODUCTION

From the first volume of Faraday's "Experimental Researches in Electricity," I quote the following passages, numbering the paragraphs as in the original text.

852. The theory of definite electrolytical or electro-chemical action appears to me to touch immediately upon the *absolute quantity* of electricity or electric power belonging to different bodies. It is impossible, perhaps, to speak on this point without committing oneself beyond what present facts will sustain; and yet it is equally impossible, and perhaps would be impolitic, not to reason upon the subject. Although we know nothing of what an atom is, yet we cannot resist forming some idea of a small particle, which represents it to the mind; and though we are in equal, if not greater, ignorance of electricity, so as to be unable to say whether it is a particular matter or matters, or mere motion of ordinary matter, or some third kind of power or agent yet there is an immensity of facts which justify us in believing that the atoms of matter are in some way endowed or associated with electrical powers, to which they owe their most striking qualities, and among them their mutual chemical affinity. As soon as we perceive, through the teaching of Dalton, that chemical powers are, however varied the circumstances in which they are exerted, definite for each body, we learn to estimate the relative degree of force which resides in such bodies; and when upon that knowledge comes the fact, that the electricity, which we appear to be capable of loosening from its habitation for a while, and conveying from place to place, *while it retains its chemical force*, can be measured out, and being so measured is found to be *as definite in its action*

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[1] Amplified from an address before the American Chemical Society at the Toronto meeting.

as any of *those portions* which, remaining associated with the particles of matter, give them their *chemical relation*, we seem to have found the link which connects the proportion of that we have evolved to the proportion of that belonging to the particles in their natural state.

855. Considering this close and twofold relation, namely, that without decomposition transmission of electricity does not occur; and, that for a given definite quantity of electricity passed, an equally definite and constant quantity of water or other matter is decomposed—considering also that the agent, which is electricity, is simply employed in overcoming electrical powers in the body subjected to its action—it seems a probable, and almost a natural consequence, that the quantity which passes is the *equivalent* of, and therefore equal to, that of the particles separated; *i. e.*, that if the electrical power which holds the elements of a grain of water in combination, or which makes a grain of oxygen and hydrogen in the right proportions unite into water when they are made to combine, could be thrown into the condition of a *current*, it would exactly equal the current required for the separation of that grain of water into its elements again.

856. This view of the subject gives an almost overwhelming idea of the extraordinary quantity or degree of electric power which naturally belongs to the particles of matter; but it is not inconsistent in the slightest degree with the facts which can be brought to bear on this point. To illustrate this I must say a few words on the voltaic pile.[1]

877. The identity of the force constituting the voltaic current or electrolytic agent, with that which holds the elements of electrolytes together (855), or in other words with chemical affinity, seemed to indicate that the electricity of

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[1] By the term voltaic pile, I mean such apparatus or arrangement of metals as up to this time have been called so, and which contain water, brine, acids, or other aqueous solutions or decomposable substances (476) between their plates. Other kinds of electric apparatus may be hereafter invented, and I hope to construct some not belonging to the class of instruments discovered by Volta.

the pile itself was merely a mode of exertion, or exhibition, or existence of *true chemical action*, or rather of its cause; and I have consequently already said that I agree with those who believe that the *supply* of electricity is due to chemical powers (857).

916. In order to render more distinct the principles which I have been endeavoring to establish, I will restate them in their simplest form, according to my present belief. The electricity of the voltaic pile (856, note) is not dependent either in its origin or its continuance upon the contact of the metals with each other (880, 915). It is entirely due to chemical action (882), and is proportionate in its intensity to the intensity of the affinities concerned in its production (908); and in its quantity to the quantity of matter which has been chemically active during its evolution (869). This definite production is again one of the strongest proofs that the electricity is of chemical origin.

917. As *volta-electro-generation* is a case of mere chemical action, so *volta-electro-decomposition* is simply a case of the preponderance of one set of chemical affinities more powerful in their nature, over another set which are less powerful: and if the instance of two opposing sets of such forces (891) be considered, and their mutual relation and dependence borne in mind, there appears no necessity for using, in respect to such cases, any other term than chemical affinity (though that of electricity may be very convenient) or supposing any new agent to be concerned in producing the results; for we may consider that the powers at the two places of action are in direct communion and balanced against each other through the medium of the metals (891), in a manner analogous to that in which mechanical forces are balanced against each other by the intervention of the lever (1031).

918. All the facts show us that the power commonly called chemical affinity, can be communicated to a distance through the metals and certain forms of carbon; that the electric current is only another form of the forces of chemical affinity; that its power is in proportion to the chemical affin-

ities producing it; that when it is deficient in force it may be helped by calling in chemical aid, the want in the former being made up by an equivalent of the latter; that, in other words, *the forces termed chemical affinity and electricity are one and the same.*

947. We seem to have the power of deciding to a certain extent in numerous cases of chemical affinity (as of zinc with the oxygen of water, etc.) which of *two modes of action of the attractive power* shall be exerted (996). In the one mode we can transfer the power onwards, and make it produce elsewhere its equivalent of action (867, 917); in the other it is not transferred, but exerted wholly at the spot. The first is the case of voltra-electric excitation, the other ordinary chemical affinity; but both are chemical actions and due to one force or principle.

959. With reference to the other set of cases, namely, those of local action (947) in which chemical affinity being exerted causes no transference of the power to a distance where no electric current is produced, it is evident that forces of the most intense kind must be active, and in some way balanced in their activity, during such combinations; these forces being directed so immediately and exclusively towards each other, that no signs of the powerful electric current they can produce become apparent, although the same final state of things is obtained as if that current had passed. It was Berzelius, I believe, who considered the heat and light evolved in cases of combustion as the consequences of this mode of exertion of the electric powers of the combining particles. But it will require a much more exact and extensive knowledge of the nature of electricity, and the manner in which it is associated with the atoms of matter, before we can understand accurately the action of this power in thus causing their union, or comprehend the nature of the great difference which it represents in the two modes of action just distinguished. We may imagine, but such imaginations must for the time be classed with the great mass of *doubtful knowledge* (876), which we ought rather to strive to diminish than to increase,

for the very extensive contradictions of this knowledge by itself shows that but a small portion of it can ultimately prove true.[1]

960. Of the two modes of action in which chemical affinity is exerted it is important to remark, that that which produces the electric current is as *definite* as that which causes ordinary chemical combinations; so that in examining the *production* or *evolution* of electricity in cases of combination or decomposition, it will be necessary, not merely to observe certain defects dependent upon a current of electricity, but also their *quantity*; and though it may often happen that the forces concerned in any particular case of chemical action may be partly exerted in one mode and partly in the other, it is only those which are efficient in producing the current that have any relation to voltaic action. Thus, in the combination of oxygen and hydrogen to produce water, electric powers to a most enormous amount are for the time active (861, 873); but any mode of examining the flame which they form during energetic combination, which has as yet been devised, has given but the feeblest traces. These therefore may not, cannot, be taken as evidences of the nature of the action; but are merely incidental results, incomparably small in relation to the forces concerned, and supplying no information of the way in which the particles are active on each other, or in which their forces are finally arranged.

961. That such cases of chemical action produce no *current of electricity*, is perfectly consistent with what we know of the voltaic apparatus, in which it is essential that one of the combining elements shall form part of, or be in direct relation with, an electrolytic conductor (921, 923). That such cases produce no *free electricity of tension*, and that when they are converted into cases of voltaic action they produce a current in which the opposite forces are so equal as to neutralize each other, prove the equality of the forces in the

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[1] Refer to 1738, Series XIV.

opposed acting particles of matter, and therefore the equality of electric power in those quantities of matter which are called *electrochemical equivalents* (824). Hence another proof of the definite nature of electrochemical action (783, etc.), and that chemical affinity and electricity are forms of the same power (917, etc.).

1031. All these effects of retardation, exhibited by decomposition against surfaces for which the evolved elements have more or less affinity, or are altogether deficient in attraction, show generally, though beautifully, the chemical relations and source of the current, and also the balanced state of the affinities at the places of excitation and decomposition. In this way they add to the mass of evidence in favor of the identity of the two; for they demonstrate, as it were, the antagonism of the *chemical powers* at the electromotive part with the *chemical powers* at the interposed parts; they show that the first are *producing* electric effects, and the second *opposing* them; they bring the two into direct relation; they prove that either can determine the other, thus making what appears to be cause and effect convertible, and thereby demonstrating that both chemical and electrical action are merely two exhibitions of one single agent or power (916, etc.).

1737. That the different modes in which electrical excitement takes place will some day or other be reduced under one common law can hardly be doubted, though for the present we are bound to admit distinctions. It will be a great point gained when these distinctions are not removed, but understood.

1738. The strict relation of the electrical and chemical powers renders the chemical mode of excitement the most instructive of all, and the case of two isolated combining particles is probably the simplest that we possess. Here however the action is local, and we still want such a test of electricity as shall apply to it, to cases of current electricity, and also to those of static induction. Whenever by virtue of the previously combined condition of some of the acting particles (923) we are enabled, as in the voltaic pile, to expand or convert the local action into a current, then chemical action can be traced through its variations to the production of *all* the phenomena of tension and the static state, these being in every respect the same as if the electric forces producing them had been developed by friction.

1739. It was Berzelius, I believe, who first spoke of the aptness of certain particles to assume opposite states when in the presence of each other (959). Hypothetically we may suppose these states to increase in intensity by increased approximation, or by heat, etc., until at a certain point combination occurs, accompanied by such an arrangement of the forces of the two particles between themselves as is equivalent to a discharge, producing at the same time a particle which is throughout a conductor (1700).

1740. This aptness to assume an excited electrical state (which is probably polar in those forming non-conducting matter) appears to be a primary fact, and to partake of the nature of induction (1162), for the particles do not seem capable of retaining their particular state independently of each other (1177) or of matter in the opposite state. What appears to be definite about the particles of matter is their assumption of a *particular* state, as the positive or negative, in relation to each other, and not of either one or other indifferently; and also the acquirement of force up to a certain amount.

1741. It is easily conceivable that the same force which causes local action between two free particles shall produce current force if one of the particles is previously in combination, forming part of an electrolyte (923, 1738). Thus a particle of zinc, and one of oxygen, when in presence of each other, exert their inductive forces (1740) and these at last rise up to a point of combination. If the oxygen be previously in union with hydrogen, it is held so combined by an analogous assertion and arrangement of the forces; and as the forces of the oxygen and hydrogen are for the time of combination mutually engaged and related, so when the superior relation of the forces between the oxygen and zinc come into play, the induction of the former or oxygen towards the metal cannot be brought on and increased without a corresponding deficiency in its induction towards the hydrogen with which it is in combination (for the amount of force in a particle is considered as definite), and the latter therefore has its force turned towards the oxygen of the next particle of water; thus the effect may be considered as extended to sensible distances, and thrown into the condition of static induction, which being discharged and then removed by the action of other particles produces currents.

1744. It seems highly probable, that excitement by friction may very frequently be of the same character. Wollaston endeavored to refer such excitement to chemical action;[1] but if by chemical action ultimate union of the acting particles is intended, then there are plenty of cases which are opposed to such a view. Davy mentions some such, and for my own part I feel no difficulty in admitting other means of electrical excitement than chemical action, especially if by chemical action is meant a final combination of the particles.

1745. Davy refers experimentally to the opposite states which two particles having opposite chemical relations can assume when they are brought into the close vicinity of each other, but *not* allowed to combine.[2] This, I think, is the first part of the action already described (1743); but in my opinion it cannot give rise to a continuous current unless combination take place, so as to allow other particles to act successively in the same manner, and not even then unless one set of the particles be present as an element of an electrolyte (923, 963); *i. e.*, mere quiescent contact alone without chemical action does not in such cases produce a *current*.

1746. Still it seems very possible that such a relation may produce a high charge, and thus give rise to excitement by friction. When two bodies are rubbed together to produce electricity in the usual way, one at least must be an insulator.

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[1] Philosophical Transactions, 1801, p. 427.

[2] Ibid., 1807, p. 34.

During the act of rubbing, the particles of opposite kinds must be brought more or less closely together, the few which are most favorably circumstanced being in such close contact as to be short only of that which is consequent upon chemical combination. At such moments they may acquire by their mutual induction (1740) and partial discharge to each other, very exalted opposite states, and when, the moment after, they are by the progress of the rub removed from each other's vicinity, they will retain this state if both bodies be insulators, and exhibit them upon their complete separation.

1747. All the circumstances attending friction seems to me to favor such a view. The irregularities of form and pressure will cause that the particles of the two rubbing surfaces will be at variable distances, only a few at once being in that very close relation which is probably necessary for the development of the forces; further, those which are nearest at one time will be further removed at another, and others will become the nearest, and so by continuing the friction many will in succession be excited. Finally, the lateral direction of the separation in rubbing seems to me the best fitted to bring many pairs of particles, first of all into that close vicinity necessary for their assuming the opposite states by relation to each other, and then to remove them from each other's influence while they retain that state.

From Helmholtz's Faraday Lecture[1] I quote the following paragraphs:

"I beg to remark that hitherto we have spoken only of phenomena. The motion of electricity can be observed and measured. Independently of this, the motion of the chemical constituents can also be measured. Equivalents of chemical elements and equivalent quantities of electricity are numbers which express real relations of natural objects and actions. That the equivalent relation of chemical elements depends on the pre-existence of atoms may be hypothetical, but we have not yet any theory sufficiently developed which can

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[1] Jour. Chem. Soc., 39, 277 (1881).

explain all the facts of chemistry as simply and as consistently as the atomic theory developed in modern chemistry.

"Now the most startling result of Faraday's law is perhaps this. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity. As long as it moves about on the electrolytic liquid, each ion remains united with its electric equivalent or equivalents. At the surface of the electrodes decomposition can take place if there is sufficient electromotive force, and then the ions give off their electric charges and become electrically neutral.

"The same atom can be charged in different compounds with equivalents of positive or of negative electricity. Faraday pointed out sulphur as being an element which can act either as anion or cation. It is anion in sulphide of silver, a cation perhaps in strong sulphuric acid. Afterwards he suspected that the deposition of sulphur from sulphuric acid might be a secondary result. The cation may be hydrogen, which combines with the oxygen of the acid, and drives out the sulphur. But if this is the case, hydrogen recombined with oxygen to form water must retain its positive charge, and it is the sulphur, which in our case must give off positive equivalents to the cathode. Therefore this sulphur of sulphuric acid must be charged with positive equivalents of electricity. The same may be applied to a great many other instances. Any atom or group of atoms which can be substituted by secondary decomposition for an ion must be capable of giving off the corresponding equivalent of electricity.

"When the positively charged atoms of hydrogen or any other cation are liberated from their combination and evolved as gas, the gas becomes electrically neutral; that is, according to the language of the dualistic theory, it contains equal quantities of positive and negative electricity; either every single atom is electrically neutralized, or one atom combines with another charged negatively. This latter assumption agrees with the inference from Avogadro's law, that the molecule of free hydrogen is really composed of two atoms.

"Now arises the question: Are all these relations between electricity and chemical combination limited to that class of bodies which we know as electrolytes? In order to produce a current of sufficient strength to collect enough of the products of decomposition without producing too much heat in the electrolyte, the substance which we try to decompose ought not to offer too much resistance to the current. But this resistance may be very great, and the motion of the ions may be very slow, so slow indeed that we should need to allow it to go on for hundreds of years before we should be able to collect even traces of the products of decomposition; nevertheless all the essential attributes of the process of electrolysis could subsist. In fact we find the most various degrees of conducting power in various liquids. For a great number of them, down to distilled water and pure alcohol, we can observe the passage of the current with a sensitive galvanometer. But if we turn to oil of turpentine, benzene, and similar substances, the galvanometer becomes silent. Nevertheless these fluids also are not without a certain degree of conducting power. If you connect an electrified conductor with one of the electrodes of a cell filled with oil of turpentine, the other with the earth, you will find that the electricity of the conductor is discharged unmistakably more rapidly through the oil of turpentine than if you take it away and fill the cell only with air.

"We may in this case also observe polarization of the electrodes as a sympton of previous electrolysis. Connect the two pieces of platinum in oil of turpentine with a battery of eight Daniells, let it stay 24 hours, then take away the battery, and connect the electrodes with a quadrant electrometer; it will indicate that the two surfaces of platinum, which were homogeneous before, produce an electromotive force which deflects the needle of the electrometer. The electromotive force of this polarization has been determined in some instances by Mr. Picker in the laboratory of the University of Berlin; he has found that the polarization of alcohol decreases with the proportion of water which it contains, and that that of the purest alcohol, ether, and oil of turpentine, is about 0.3, that of benzene 0.8 of a Daniell's element. ....."

"All these facts show that electrolytic conduction is not at all limited to solutions of acids or salts. It will, however, be rather a difficult problem to find out how far the electrolytic conduction is extended, and I am not yet prepared to give a positive answer. What I intended to remind you of was only that the faculty to be decomposed by electric motion is not necessarily connected with a small resistance to the current. It is easier for us to study the cases of small resistance, but the illustration which they give us about the connection of electric and chemical force is not at all limited to the acid and saline solutions usually employed.

"Hitherto we have studied the motions of ponderable matter as well as of electricity, going on in an electrolyte. Let us now study the forces which are able to produce these motions. It has already appeared somewhat startling to everybody who knows the mighty power of chemical forces, and the enormous quantity of heat and mechanical work which they are able to produce, how exceedingly small is the electric attraction at the poles of a battery of two Daniell's cells, which nevertheless is able to decompose water. One gram of water, produced by burning hydrogen with oxygen, develops so much heat, that this heat transformed by a steam engine into mechanical work would raise the same weight to a height of 1,600,000 meters. And on the contrary we require to use the most delicate contrivances to show that a gold leaf or a little piece of aluminum hanging on a silk fiber can be at all moved by the electric attraction of the battery. The solution of this riddle is found if we look at the quantities of electricity with which the atoms appear to be charged.

"The quantity of electricity which can be conveyed by a very small quantity of hydrogen, when measured by its electrostatic forces, is exceedingly great. Faraday saw this, and endeavored in various ways to give at least an approximate determination. He ascertained that even the most powerful batteries of Leyden jars, discharged through a voltameter, give scarcely any visible traces of gases. At present we can give definite numbers. The electrochemical equivalent of the electromagnetic unit of the galvanic current has been determined by Bunsen, and more recently by other physicists. This determination was followed by the very difficult comparison of the electromagnetic and electrostatic effects of electricity, accomplished at first by Professor W. Weber, and afterwards under the auspices of the British Association by Professor Clerk Maxwell. The result is, that the electricity of 1 mg of water, separated and communicated to two balls, 1 km distant, would produce an attraction between them equal to the weight of 26,800 kg.

"As I have already remarked, the law that the intensity of the force is inversely proportional to the quantities of attracting and of attracted mass, holds good as well in the case of gravitation as in that of electric attraction and repulsion. We may, therefore, compare the gravitation acting between two quantities of hydrogen and oxygen with the attraction of their electric charges. The result will be independent of the size and the distance of these quantities. We find that the electric force is as great as the gravitation of ponderable masses, being 71,000 billion times greater than that of the oxygen and hydrogen containing these electric charges.

"The total force exerted by the attraction of an electrified body upon another charged with opposite electricity is always proportional to the quantity of electricity contained on the attracting as on the attracted body.

"Although, therefore, the attracting forces exerted by the poles of a little battery able to decompose water on such electric charges as we can produce with our electric machines, are very moderate, the forces exerted by the same little apparatus on the enormous charges of the atoms in 1 mg of water may very well compete with the mightiest chemical affinity.

"If we now turn to investigate how the motions of the ponderable molecules are dependent upon the action of these forces, we must distinguish two different cases. At first we may ask what forces are wanted to call forth motions of the ions with their charge through the interior of the fluid; secondly, what are wanted to separate the ion from the fluid and its previous combinations?

"Let us begin with the case in which the conducting fluid is surrounded everywhere by insulating bodies. Then no electricity can enter, none can go out through its surface, but positive electricity can be driven to one side, negative to the other, by the attracting and repelling forces of external electrified bodies. This process going on as well in every metallic conductor is called 'electrostatic induction.' Liquid conductors behave quite like other metals under these conditions. Great quantities of electricities are collected, if large parts of the surfaces of the two bodies are very near to each other. Such an arrangement is called an electric condenser. We can arrange electric condensers in which one of the surfaces is that of a liquid, as Messrs. Ayrton and Perry have done lately. The water-dropping collector of electricity, invented by Sir W. Thomson, is a peculiar form of such a condenser, which can be charged with perfect regularity by the slightest electromotive force perceptible only to the most sensitive electrometer. Professor Wüllner has proved that even our best insulators, exposed to electric forces for a long time, are ultimately charged quite in the same way as metals would be charged in an instant. There can be no doubt that even electromotive forces less than 1/100 Daniell produce perfect electrical equilibrium in the interior of an electrolytic liquid.

"Another somewhat modified instance of the same effect is afforded by a voltametric cell containing two electrodes of platinum, which are connected with a Daniell's cell, the electromotive force of which is sufficient to decompose the electrolyte. Under this condition the ions carried to the electrodes cannot give off their electric charges. The whole apparatus behaves, as was first accentuated by Sir W. Thomson, like a condenser of enormous capacity. The quantity of electricity, indeed, collected in a condenser under the same electromotive force is inversely proportional to the distance of the plates. If this is diminished to 1/100, the condenser takes in 100 times as much electricity as before. Now, bringing the two surfaces of platinum and of the liquid into immediate contact, we reduce their interval to molecular distances. The capacity of such a condenser has been measured by Messrs. Varley, Kohlrausch and Colley. I have myself made some determinations which show that oxygen absorbed in the fluid is of great influence on the apparent value. By removing all traces of gas I have got a value a little smaller than that of Kohlrausch, which shows that if we divide equally the total value of the polarization between two platinum plates of equal size, the distance between the two strata of positive and negative electricity, the one lying on the last molecules of the metal, the other on those of the fluid, ought to be a ten millionth part (Kohlrausch 1/15,000,000) of a millimeter. We always come nearly to the same limit, when we calculate the distances through which molecular forces are able to act, as already shown in several other instances by Sir W. Thomson.

"Owing to the enormous capacity of such an electrolytic condenser, the quantity of electricity which enters into it, if it is charged even by a feeble electromotive force, is sufficiently great to be indicated easily by a galvanometer. What I now call charging the condenser, I have before called polarizing the metallic plate. Both, indeed, are the same process, because electric motion is always accompanied in the electrolytes by chemical decomposition.

"Observing the polarizing and depolarizing currents in a cell like that represented in Fig. 1, we can observe these phenomena with the most feeble electromotive forces of

1/1000 Daniell, and I found that down to this limit the quantity of electricity entering into the condenser was proportional to the electromotive force by which it was collected. By taking larger surfaces of platinum, I suppose it will be possible to reach a limit much lower than that. If any chemical force existed besides that of the electrical charges which could bind all the pairs of opposite ions together, and required any amount of work to be vanquished, an inferior limit ought to exist to such electromotive forces as are able to attract the ions to the electrodes, and to charge these as condensers. No phenomenon indicating such a limit has as yet been discovered, and we must, therefore, conclude that no other force resists the motions of the ions through the interior of the liquid than the mutual attractions of their electric charges. These are able to prevent the atoms of the same kind which repel each other from collecting at one place, and atoms of the other kind attracted by the former from collecting at any other part of the fluid, as long as no external electric force favors such distribution. The electric attraction, therefore, is able to produce an equal distribution of the opposite constituent atoms throughout the liquid, so that all parts of it are neutralized electrically as well as chemically. ...."

"The electrical force acting on equal quantities of electricity situated at the inside of one of the electric strata of a condenser is proportional to the electromotive force which has charged the condenser, and inversely proportional to the distance of the charged surfaces. If these are 1/100 mm apart, it is 100 times as great as if they are 1 mm apart. If we come, therefore, to molecular distances, like those calculated from the measurement of the capacity of polarized electrodes, the force is ten million times as great, and becomes able, even with a moderate electromotive force, to compete with its electric charge, and hold the atoms bound to the liquid.

"Such is the mechanism by which electric force is concentrated at the surface of the electrodes and increased in its intensity to such a degree that it becomes able to overpower the mightiest chemical affinities we know of. If this can be done by a polarized surface, acting like a condenser charged by a very moderate electromotive force, can the attractions between the enormous electric charges of anions and cations be an unimportant and indifferent part of chemical affinity?"

"Faraday very often........[expresses] his conviction that the forces termed chemical affinity and electricity are one and the same. I have endeavored to give you a survey of the facts connected with the question, and to avoid as far as possible the introduction of hypotheses, except the atomic theory of modern chemistry. I think the facts leave no doubt that the very mightiest among the chemical forces are of electric origin. The atoms cling to their electric charges, and opposite electric charges cling to each other; but I do not suppose that other molecular forces are excluded, working directly from atom to atom. Several of our leading chemists have lately begun to distinguish two classes of compounds, *viz.*, molecular aggregates and typical compounds, the latter being united by atomic affinities, the former not.

"Electrolytes belong to the latter class. If we conclude from the facts that every unit of affinity is charged with one equivalent either of positive or of negative electricity, they can form compounds, being electrically neutral only if every unit charged positively unites under the influence of a mighty electric attraction with another unit charged negatively. You see that this ought to produce compounds in which every unit of affinity of every atom is connected with one and only one other unit of another atom. This, as you will see immediately, is the modern chemical theory of quantivalence, comprising all the saturated compounds. The fact that even elementary substances, with few exceptions, have molecules composed of two atoms, makes it probable that even in these cases electric neutralization is produced by the combination of two atoms, each charged with its full electric equivalent, not by neutralization of every single unit of affinity.

"Unsaturated compounds with an even number of unconnected units of affinity offer no objection to such an hypothesis; they may be charged with equal equivalents of opposite electricity. Unsaturated compounds with one unconnected unit, existing only at high temperatures, may be explained as dissociated by intense molecular motion of heat in spite of their electric attractions. But there remains one single instance of a compound which, according to the law of Avogadro, must be considered as unsaturated even at the lowest temperature, namely, nitric oxide (NO), a substance offering several very uncommon peculiarities, the behavior of which will be perhaps explained by future researches."

In 1901 Nernst made an address[1] at the annual meeting of the German Electrochemical Society on "The Importance of Electrical Methods and Theories for Chemistry."

"The modern physical investigations on electricity, which are chiefly concerned with electrical oscillations, ought not to mislead one into the often heard opinion that electricity is to be explained as a state of oscillations. This is like supposing that one learns something final about the nature of air by studying the vibrations in acoustic experiments. It is more true to say that the investigations, referred to, have not in any way invalidated the fluid theory of electricity, *i. e.*, the conception of electricity as a substance. Electrochemistry is probably destined to carry us farther along this path.

"The field of electrochemistry is that of the formation and destruction of ions, just as that of chemistry is the change from atoms to molecules and back. In consequence of the properties of water, ions are formed chiefly in that solvent and aqueous solutions are therefore the chief subject of electrochemical investigation.

"For the investigation of solutions containing ions, we make use not only of all the purely chemical methods, but also of all those which are concerned with the electrical charge on the ions. By an application of the van't Hoff-Avogadro rule Arrhenius has shown how to determine the concentration of the ions as well as of the neutral molecules; Hittorf has

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[1] Zeit. Elektrochemie, 7, 1005 (1901).

established the constitution of the ions and their identity with the chemical radicals; Kohlrausch has measured their rate of migration; and Ostwald, by means of these methods, has obtained an exact measure of the strength of acids.

"The speaker's methods of determining the concentration of the ions of a metal by measuring the difference of potential between the metal and the solution, have led to the quantitative determination of amounts smaller even than those which can be detected by spectrum analysis. Ostwald, and also Arrhenius, have determined the phenomenally low degree of electrolytic dissociation of water, an exceptionally important chemical constant.

"While these methods enable us to get at the nature of the ions in very different ways, electricity also gives us the means of separating chemical compounds into their components for, by electrolysis the ions are deprived of their charges and are precipitated in a neutral form. The potential difference employed overcomes the force which tends to keep the ions as such; and since one can increase the applied potential difference indefinitely, one may overcome the strongest chemical affinities. Thus Davy succeeded in isolating the alkali metals by electrolysis and Moissan prepared fluorine.

"If on the other hand a substance, such as a metal for instance, forms ions when dissolving, there must be a displacement of electricity which is the source of the voltage of the voltaic cell (theory of Nernst). Such displacements of electricity also occur during many simple chemical reactions, such as the dissolving of a metal in an acid, where the electrical charges pass from the hydrogen, which had been present as ion, to the metal which now is transformed into ions.

"One is therefore tempted to make the assumption that all chemical forces are of electrical nature. A far-reaching analogy between chemical and electrical processes certainly exists; for the chemical reaction velocity is proportional to the driving affinity and is inversely proportional to the chemical resistance, corresponding to a kind of Ohm's law. In consequence the electromotive force of a voltaic cell must be looked upon as a measure of the affinity of the chemical reactions taking place in the cell. This electrical method of measuring chemical affinity is not the only one we have but, whenever applicable, it is the most accurate and the most convenient.

"Of course this does not prove in any way that the chemical forces are actually of electrical nature, and people have advanced the view that such a question is an utter waste of time and that one knows enough when one determines the magnitude of the affinity. Yet an investigator ought not to be frightened by an apparently bold attempt to discover the mechanism of the processes. It is certainly justifiable for one to ask whether a machine is driven by steam, water or electricity even if one already knows that it will give so many horse-power.

"Berzelius's theory of chemical affinity looked upon all compounds as dualistic and as consisting of a positively and a negatively electrical radical. It could not hold its own during the development of organic chemistry when a monistic view, based on the theory of valence, proved more serviceable for a large class of compounds. To-day both views appear to have a justification for one recognizes substances forming positive and negative ions, *i. e.*, elements and radicals which after combining are able to take up corresponding charges of electricity under suitable conditions. But while Berzelius wished to explain the strength of affinity by the amount of the charges, we know, from Faraday's results, that equivalent quantities even of elements differing most widely in affinity carry exactly equal charges of electricity. This surprising fact finds a plausible explanation if we adopt a suggestion by Helmholtz and consider electricity as a substance of atomic structure consisting of positive and negative electrons, in which case we consider the ions as chemical compounds of the elements with such electrons. We are also led to such a chemical theory of electricity by entirely different investigations on which Kaufmann reported in his address and from which it appears that the atomic weight of the negative electrons is about 0.0005. The peculiarities of the two electron elements, which distinguish them from all others, are the special manifestations of force which are so different from an attraction and which determine their individuality just as much as other properties characterize the special nature of the other elements.

"The conception of ions as saturated chemical compounds of atom and electron leads everywhere to real consequences. Thus sodium ions are just as different from the element as sodium chloride for instance. In the molecular compounds of Werner's theory, the saturated ammonia molecules are replaceable by ions and behave chemically in an analogous manner. Similar developments are to be found in the papers of Abegg and Bodländer.

"The final conclusion from this point of view, namely the existence of a compound of the positive and negative electron, cannot be tested as yet owing to the lack of a suitable 'reagent;' but this molecule may play an important part in the world of the light-ether.

"The relation between the monistic and the dualistic points of view may be formulated somewhat as follows: all elements or radicals have an affinity for positive or negative electrons with which they form ions. They also have a non-polar attraction for each other. This last determines, for instance, the combination of two hydrogen atoms to form hydrogen molecules; also the existence of phosphorus sulphide, iodine chloride, etc.; the existence of metal compounds; and especially the existence of carbon compounds.

"When positive and negative elements combine there is also the addition of an electron molecule which splits up when ions are formed, and it appears especially remarkable that such compounds, obviously in consequence of the addition of an electron molecule, differ surprisingly more from the components than do the compounds of similar elements where there appears to be no taking up of an electron molecule. Thus the compounds of the metals are metallic, those of the metalloids are non-metallic while the combination of sodium and chlorine, for instance, gives rise to a salt having entirely novel properties.

"It is also possible that there are elements which react with the positive electron alone without its being necessary for any other element to take up the negative electron. In this case the negative electron will be set free and will appear in the Becquerel rays.

"Though this chemical theory of electricity is far from being a finished structure, it has its justification in that it gives a new impetus to investigation."

While this theory of Nernst rests on the work of Faraday and of Helmholtz, it opens up a new field. Nernst is interested in the chemical theory of electricity, the chief applications of which are to aqueous solutions. In fact Nernst explicitly excludes the carbon compounds in general as being the result of a non-polar attraction. Faraday and Helmholtz, on the other hand, were especially interested in the problem whether all chemical affinity might not be electrical in nature. While it may be that Nernst's limitation is a necessary one, it is not one to be accepted until we have to. Personally, I think that there is yet a great deal of work to be done along the lines laid down by Faraday and Helmholtz as well as along those laid down by Nernst.

The dualistic theory of Berzelius was weak in two points. There was apparently no way of bringing the chloracetic acids into harmony and Berzelius made the mistake of postulating that the electrical charges were proportional to the affinity. While this was the simplest assumption to make, it was not the only one that might be made and it was not necessary to a dualistic theory. Faraday's experiments showed that the assumption was wrong and also showed what assumption should have been made. The difficulty disappears if we say that the voltage necessary to remove the charge from the ion is a measure of the affinity. If one prefers, one may say that the attraction of the ion for the electrical charge is proportional to the affinity. This last is

Helmholtz's formulation. With this modification the theory of Berzelius becomes applicable to all ion reactions.

The fundamental weakness of the theory of Berzelius lay in its inability to deal with the substitution phenomena of organic chemistry. So long as chlorine is looked upon as always a negative radical and hydrogen as always a positive radical, the replacement of one by the other without a marked change of properties is clearly absurd. If, however, we postulate that chlorine may be positive at times or hydrogen negative, the theory of Berzelius becomes formally applicable to substitutions in organic chemistry. It may well be a question whether such a modification does not make the theory so vague as to be worthless. This is a question which I do not intend to discuss at present. I do wish to call attention to the fact that this very hypothesis has been put forward as a result of recent investigations in physical chemistry.

As a consequence of measurements on the rate of oxidation of phosphorus, sulphur and aldehyde, van't Hoff was induced to postulate the existence of positively and negatively charged oxygen atoms.[1] "The chief result obtained by Mr. Ewan in his work in my laboratory on the rate of oxidation of phosphorus, sulphur and aldehyde, is that after the oxidation begins (and below the mysterious limiting oxygen pressure at which the reaction is checked) the rate is very closely proportional to the square root of the oxygen pressure. This relation suggests the thought that during this slow oxidation it is not the oxygen as such which is active but the exceedingly small amount of the dissociation products which are possibly present. If we are dealing with an equilibrium corresponding to the equation

$$O_2 \rightleftarrows 2O$$

the rate would be proportional to the square root of the oxygen pressure. This is the view advocated by Mr. Ewan.

"Now the question comes up whether this is a dissociation into atoms or into ions, *i. e.*, respectively positively and

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[1] Zeit. phys. Chem., 16, 411 (1895).

negatively charged ions. If one adopts the latter hypothesis, one must evidently take up the question of ozone, though in a somewhat different way than heretofore. According to views often expressed, the oxygen molecule might be half used up for slow oxidation while the remaining half might react to form ozone. According to the above proportionality with the square root of the pressure, the dissociation is not a consequence of the oxidation but probably occurs from the beginning. If there are oppositely charged dissociation products, it is quite intelligible that the oxidizable substance might react more readily with one while the remainder might give the oxygen an electrical charge which might be compensated by a secondary reaction, such as ozone formation, decolorization of indigo, etc.

"There are indications of all this in the literature. The cloud formation, for instance, during the oxidation of phosphorus is due essentially to the condensation of water vapor and occurs also in air which has been in contact with phosphorus and has then been freed from ozone by means of potassium iodide. It reminds one therefore very much of the cloud formation which Helmholtz has observed in water vapor under electrical influences. Later, it will be shown that the primary product in oxygen 'made active' by phosphorus is not ozone because it checks the luminescence of phosphorus while ozone increases it. The primary product may therefore be electrically charged oxygen."

Stieglitz[1] has assumed the existence of chlorine cations in the reaction between hypochlorous and hydrochloric acids. From experiments with non-aqueous solvents Walden[2] deduces the existence of univalent and trivalent bromine and iodine cations, of trivalent and pentavalent phosphorus cations, and of the bivalent cations S_2''. In a paper on valency, Abegg says:[3]

"A third criterion for the existence of finite ion con-

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[1] Jour. Am. Chem. Soc., 23, 796 (1901).

[2] Zeit. phys. Chem., 43, 385 (1903).

[3] Zeit anorg. Chem., 39, 339, 375 (1904).

centrations is to be found in a rapid chemical reaction with other ions, such as those of water in hydrolysis, when most probably either the hydrogen or the hydroxyl ions react with the oppositely charged ions of the compound, thus showing their existence. Thus through the hydroxyl ions of water or of the alkalies, many chlorides are decomposed with formation of hydrochloric acid and the hydroxyl compound of the element with which the chlorine was combined, showing thereby that the element acted as a cation. By the formation of hydrogen sulphide in aqueous solution, many sulphides show the positive nature of the element combined with the sulphur as in the case of B_2S_3, P_2S_3, etc. Beside the cations $Be^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Sn^{\cdot\cdot}$, etc., which occur in measurable quantities, the indirect proof of the existence of the cations $Sn^{\cdot\cdot\cdot\cdot}$, $Pb^{\cdot\cdot\cdot\cdot}$, $B^{\cdot\cdot\cdot}$, $Ti^{\cdot\cdot\cdot\cdot}$, $Si^{\cdot\cdot\cdot\cdot}$, $As^{\cdot\cdot\cdot}$, $P^{\cdot\cdot\cdot}$, $S_2^{\cdot\cdot}$, $I^{\cdot\cdot\cdot}$ and many others is shown by the formation of hydroxyl compounds. In the same way the reaction with the hydrogen ion of water or of acids shows the existence of the negative ions C_2'' in the carbides, of N''' in the nitrides, of P_2'''' in the phosphides, of As''' in the arsenides, of Sb''' in the antimonides, since hydrogen compounds are formed on decomposition. Especially noticeable is the fact that Mg_2Si is decomposed even by dilute acids and Mg_3B_2 only by concentrated strong acids with formation of silicon and boron hydrides respectively. This shows gradations in the negative electro-affinity such that the boride contains boron anions than the silicide does silicon anions because a higher concentration of hydrogen ions is necessary to cause decomposition.

"The study of the decomposition furnishes usually an entirely definite means of determining the polar rôle of the components of a compound. Thus it might be doubtful, at first sight, whether iodine or chlorine were the positive element in such a compound as iodine monochloride. The products of hydrolysis enable us to distinguish at once. There are formed hydrochloric acid and iodine oxyacids; therefore the hydroxyl ion of the water has gone to the iodine and the hydrogen ion to the chlorine. The iodine is therefore the positive component and the chlorine the negative component; the compound should be called iodine chloride and not chlorine iodide.

"The metal hydrides present another interesting case. Moissan concluded from their not conducting electricity that —to use our phraseology—the hydrogen played the part of a metalloid. This reasoning is obviously not binding because we know that electrolytic conductivity is a characteristic of compounds having components with different polarity. What Moissan thought he had shown from the absence of metallic conductivity, can be deduced more directly from his observations on the decomposition of the hydrides by water. The metals take the hydroxyl ion and are therefore the positive components. The hydrogen of the hydrides combine with the hydrogen ion of the water to form hydrogen molecules and we thus become familiar with a compound H'H' containing chemically identical atoms with opposite polarity.

"Now fundamentally every reaction is a metathetical one, with organic compounds no less than with electrolytes and we have already considered the transition cases (preceding three paragraphs). There is no doubt but that the introduction of elements or radicals of marked polarity (metals, oxygen, halogens, etc.) into organic compounds increases the reactivity of these substances extraordinarily. We may account for this by saying that atoms or atom groups form very inert compounds with hydrogen or carbon for instance when neither of the two partners differs markedly in polarity; but that they become active when they are forced into a marked polar contrast by the presence of a strongly polar substitution product. As a simple illustration of this, $CH_3.H$ does not react with HCl because there is not a sufficient difference of polarity between CH_3 and H. On the other hand, $CH_3.OH$ reacts with HCl because the negative OH makes the radical CH_3 more positive by contrast. The products of the double decomposition are CH_3Cl and H_2O. CH_3 reacts differently when it is combined with a metal ($Zn(CH_3)_2$ for instance); it then becomes the negative component and the reaction products are the metallic chloride and $CH_3.H$. The result of the reaction may thus be different; in connection with this the important thing is the inter-relation between the reactivity of the molecule and the difference of polarity of its parts. It is almost superfluous to add that the molecule splits the point where the polarity changes, this however depending in the case of chemical equilibrium upon the other molecules entering into the reaction and upon the arrangement of polarity in the reaction products."

The conclusions of Abegg and Stieglitz are not necessarily correct. They rest on the assumption that all reactions are ion reactions, which has certainly not yet been established. There is also an unexplained change from electrolytic to metallic conductivity in Abegg's criticism of Moissan's conclusions in regard to the hydrides. Nernst does not accept Abegg's conclusions and looks upon the formation of hydrogen gas as due to a non-polar union. The recent work of Kraus,[1] however, furnishes a strong argument in favor of Abegg's views. In liquid ammonia as solvent, the compound $NaPb_2$ is apparently an electrolyte with sodium as cation and Pb_2' as anion. For the present, it is immaterial which view one holds because it is impossible to apply the theory of Berzelius effectively until we know a good deal more than we do now about the conditions under which a given substance can change from being charged positively to being charged negatively or *vice-versa*. The really important thing about it all is that the phenomena which wrecked the theory of Berzelius are still stumbling blocks to us to-day. The theory of valence shoved the difficulties back for fifty years or more but it did not do away with them.

II. MEASUREMENT OF CHEMICAL AFFINITY

Since Helmholtz delivered his Faraday lecture, there has been a great change in regard to our knowledge of chemical affinity. People have become familiar with the theorem of Gibbs[2] that the electromotive force of a completely reversible

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[1] Jour. Am. Chem. Soc., 29, 1563 (1907).

[2] Thermodynamische Studien, 390

cell is equal to the difference of the chemical potentials. The theory of the inversion cell has been worked out by van't Hoff[1] and a number of cases have been studied quantitatively. These cases may be grouped under seven heads.

1. Precipitation of a Metal by a Metal

The simplest case is that in which there is only one solution, as in cells of the Clark type. These cells are completely reversible if we neglect the infinitesimal solubility of the mercurous sulphate. It should be remembered that the electromotive force of the cell is a measure of the chemical affinities involved in the reactions actually taking place. In the cell

$$Zn \mid ZnSO_4, \underline{Hg_2SO_4} \mid Hg$$

the reaction is[2]

$$Zn + Sol_1.ZnSO_4 + Hg_2SO_4 = Sol_2.ZnSO_4 + 2Hg$$

and not

$$Zn + Hg_2SO_4 = ZnSO_4 + 2Hg.$$

If the solution is saturated with respect to zinc sulphate, the reaction is

$$Zn + Sol_1.ZnSO_4 + Hg2SO_4 = Sol_2.ZnSO_4 + (1 + x)ZnSO_4 7H_2Ox + 2Hg.$$

What the reaction is in these cases was first pointed out clearly by Cohen.[3]

The Daniell cell may be taken as typical of the two-solution cells. This cell is not strictly reversible because of the inter-diffusion of the two solutions which is not reversible electrolytically. The electromotive force, as measured, includes the diffusion potential for the two solutions. In many cases this may be neglected; but in accurate work a correction must be applied. After correcting for the difference of

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[1] Cf. Cohen: Studien zur chemischen Dynamik, 260.

[2] $Sol_1.ZnSO_4$ is used to denote the initial solution of zinc sulphate while $Sol_2.ZnSO_4$ is the resultant solution.

[3] Zeit. phys. Chem., 34, 62 (1900).

potential between the solutions, the electromotive force is a measure of the chemical affinity for the reaction

$$Zn + Sol_1.ZnSO_4 + Sol_1.CuSO_4 = Sol_3.ZnSO_4 + Sol_4.CuSO_4 + Cu.$$

This is not the same reaction which takes place when a piece of metallic zinc is dipped into a copper sulphate solution. Quite apart from the possible formation of an alloy, the chemical reaction involves the formation of zinc sulphate in a solution of copper sulphate containing no zinc sulphate. The chemical affinity involved is that of the reaction

$$Zn + Sol_1.CuSO_4 = Sol_2(ZnSO_4, CuSO_4) + Cu.$$

Going back to the Daniell cell and changing the concentrations of the zinc sulphate and the copper sulphate solutions, we change the chemical affinity and consequently the electromotive force.[1] Increasing the concentration of the zinc sulphate or decreasing the concentration of the copper sulphate decreases the electromotive force of the cell. If these changes in concentration could be made sufficiently great, the electromotive force would pass through zero and its sign would then reverse, showing that copper was now the anode and zinc the cathode. The solubility of zinc sulphate determines the maximum concentration of that salt. Theoretically it should be possible to reverse the cell by diluting the copper sulphate solution indefinitely; but this is not feasible practically, because the moment the circuit is closed even for an instant enough copper will go into solution to change things back. The same result can be accomplished by adding potassium cyanide in excess to the copper sulphate solution. There is formed potassium cuprous cyanide and potassium sulphate. This experiment shows that the potential difference between a metal and a solution of a salt of that metal does not necessarily depend on the absolute amount of that salt in solution. Further experiments have shown that one of the factors on which the potential difference depends is the concentration of the metal as ion,[2] using Faraday's definition that the

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[1] Nernst: Zeit. phys. Chem., 4, 178 (1889).

[2] Nernst: Ibid., 4, 148 (1889).

substances carried to anode and cathode by the current are the anions and cations respectively.

In the cell

$$Cu \mid KCu(CN)_2, KCN \mid ZnSO_4 \mid Zn$$

the reaction involved is

$$Cu + Sol_1.KCu(CN)_2,KCN + Sol_1.ZnSO = Sol_2.KCu(CN)_2,KCN,K_2SO_4 + Sol_2.ZnSO_4,K_2SO_4 + Zn.$$

The reaction in this case is one which it would be very difficult, perhaps impossible, to duplicate chemically.

One must be on one's guard against a possible error which can easily occur with nickel and copper for instance. If one takes the ordinary solutions, containing air and measures the cell

$$Ni \mid NiSO_4 \mid CuSO_4 \mid Cu,$$

one gets almost no electromotive force. This is not because the reaction

$$Ni + Sol_1NiSO_4 + Sol_1CuSO_4 = Sol_2.NiSO_4 + Sol_2.CuSO_4 + Cu$$

corresponds to a zero chemical affinity. It is because that reaction does not take place under the conditions described. The nickel becomes passive and is not attacked. In a case of this sort, it is advisable to determine decomposition voltages instead of electromotive forces. It is to this peculiarity of nickel that we owe the results obtained by Carhart[1] with a so-called nickel sulphate concentration cell. The work of Euler[2] and of Siemens[3] showed that it was not easy to determine accurately the potential difference between nickel and a nickel sulphate solution. The discrepancy between Le-Blanc's[4] values for the decomposition voltage of cobalt sulphate and Neumann's[5] values for the potential difference between cobalt and cobalt sulphate is probably due to a similar cause.

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[1] Trans. Am. Electrochem. Soc., 1, 105 (1902).

[2] Zeit. anorg. Chem., 41, 93 (1904).

[3] Ibid., 41, 264 (1904).

[4] Zeit. phys. Chem., 12, 345 (1893).

[5] Ibid., 14, 222 (1894).

2. Allotropic Forms of Metals

Cohen[1] has measured the difference of potential between the two forms of tin when dipped in a solution of a tin salt.

3. Amalgam Cells

If zinc amalgams of two concentrations are made electrode with a zinc salt as an electrolyte, the theorem of Le-Chatelier shows us that a current will tend to flow in such a direction as to equalize the concentrations in the two amalgams. The quantitative relations were first studied by v. Turin[2] and by G. Meyer.[3]

4. Stable and Instable Salts.

If we construct a cell such as

$$\mathrm{Zn} \mid \overset{\text{Sat. solution}}{\mathrm{ZnSO_4 7H_2O}} \mid \overset{\text{Sat. solution}}{\mathrm{ZnSO_4 6H_2O}} \mid \mathrm{Zn}$$

or

$$\mathrm{Hg} \mid \overset{\text{Sat. solution}}{\underline{\mathrm{Hg_2SO_4}}\mathrm{Na_2SO_4}} \mid \overset{\text{Sat. solution}}{\mathrm{Na_2SO_4 10H_2O}\underline{\mathrm{Hg_2SO_4}}} \mid \mathrm{Hg}$$

the current will flow in such a direction as to eliminate the instable salt. Only at the inversion temperature does the tendency to change and the electromotive force become zero.[4]

5. Metathetical Reactions

We can measure the chemical affinity of such a reaction as

$$\underline{\mathrm{TlCl}} + \mathrm{KSCN} = \underline{\mathrm{TlSCN}} + \mathrm{KCl}$$

by arranging a cell[5]

$$\text{Tl amalgam} \mid \underline{\mathrm{TlSCN}},\ \mathrm{KSCN} \mid \mathrm{KCl}\ \underline{\mathrm{TlCl}} \mid \text{Tl amalgam.}$$

By changing the relative concentrations of potassium sulphocyanate and potassium chloride the current can be

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[1] Zeit. phys. Chem., 30, 623 (1899).

[2] Ibid., 5, 340 (1890); 7, 221 (1891).

[3] Wied. Ann., 40, 244 (1890); Zeit. phys. Chem., 7, 477 (1891).

[4] Cohen: Zeit. phys. Chem., 14, 53 (1894); 25, 300 (1894). Cohen and Bredig: Ibid., 15, 535 (1894); 16, 453 (1895).

[5] Knüpffer: Ibid., 26, 255 (1898).

made to flow in either direction. Another interesting case, illustrating the same principle, is the cell:

$$\mathrm{Pb} \mid \underline{\mathrm{PbSO_4}}\ \mathrm{K_2SO_4} \mid \mathrm{KI}\ \underline{\mathrm{PbI_2}} \mid \mathrm{Pb}.$$

This corresponds to the reversible reaction[1]

$$\underline{\mathrm{PbI_2}} + \mathrm{K_2SO_4} = \underline{\mathrm{PbSO_4}} + 2\mathrm{KI}.$$

6. Oxidation and Reduction Cells

If we dip one platinum electrode into a solution of a reducing agent, R, and another electrode into a solution of an oxidizing agent, O, we get two half cells which may be measured against each other or against a standard electrode. In the cell

$$\mathrm{Pt} \mid \mathrm{R} \mid \mathrm{O} \mid \mathrm{Pt}$$

the current flows through the cell from the reducing agent to the oxidizing agent.[2] If the reactions are completely reversible the electromotive force is a measure of the chemical affinity. Ferrous and ferric chlorides are types of reversible reducing and oxidizing agents. On the other hand pyrogallol in alkaline solution is a powerful reducing agent but not a reversible one. We can reduce potassium chlorate to chloride, but we cannot oxidize it back again directly. The gas cells are special cases of reduction and oxidation cells but here we have very distinct difficulties; the so-called excess voltage[3] giving all the effects of non-reversibility. There is one other point of interest about these cells, that the reaction in the cell is not necessarily the same that would take place if the solutions were mixed. If we take the cell

$$\mathrm{Pt} \mid \mathrm{Na_2S} \mid \mathrm{NaAc} \mid \mathrm{AgAc} \mid \mathrm{Pt}$$

we shall get the formation of metallic silver at the cathode, whereas we get silver sulphide if the solutions are mixed.

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[1] Klein: Zeit. phys. Chem., 36, 361 (1901).

[2] Bancroft: Ibid., 10, 387 (1892); Neumann: Ibid., 14, 226 (1894). Peters: Ibid., 26, 193 (1898).

[3] Caspari: Zeit. phys. Chem., 30, 89 (1899); Coehn and Osaka: Zeit. anorg. Chem., 34, 86 (1903).

7. Action of Light

The effect of light on silver chloride is to cause a reduction and a partial evolution of chlorine. The amount of this decomposition and the change in chemical affinity, caused by the light, can easily be measured electrically,[1] so that here also we get quantitative data.

In addition to the electrical methods of measuring chemical affinity, we have also non-electrical methods. Suppose we have equilibrium for a dissociating gas with known partial pressures, or for a dissociating solute with the partial osmotic pressures known. Knowing these data and the equilibrium formula we can calculate the work that would be done if we could displace the equilibrium mechanically. A measure of the work done in displacing an equilibrium reversibly is a measure of the chemical affinity and of the electromotive force that would be generated if the reaction could be made to take place in a voltaic cell. Since the work done in displacing the equilibrium depends on the equilibrium (or dissociation) constant, it follows that there must be a relation between the equilibrium constant and the electromotive force. This relation was formulated by van't Hoff[2] in 1886. If we write the equation for equilibrium in this form

$$\log \mathrm{K} = \Sigma n \log c$$

the van't Hoff relation between free energy, F, electromotive force, E, and the equilibrium constant takes the form

$$\mathrm{F} = 96600\,\mathrm{E} = \mathrm{RT}(\log \mathrm{K} - \Sigma n \log c)$$

where c is used to denote concentrations which may differ from the equilibrium concentrations C. If we arbitrarily make the concentrations of all the reacting substances equal to unity, the term $\Sigma\ n \log c$ disappears and our formula becomes

$$\mathrm{F} = 96600\,\mathrm{E} = \mathrm{RT} \log \mathrm{K}.$$

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[1] Luggin: Zeit. phys. Chem., 23, 577 (1899); Luther: Ibid., 30, 628 (1899); Wildermann: Ibid., 41, 87; 42, 257 (1902); 52, 209 (1905); Phil. Trans., 199*A*, 337 (1902); 206*A*, 335 (1906).

[2] Cf. Bredig: Zeit. Elektrochemie, 4, 544 (1898).

This is a very popular way of writing the formula; but my experience is that it is rather confusing and that there is no advantage to be gained by this particular transformation. This formula has been tested experimentally for the precipitation of a metal by a metal; for amalgam cells; for stable and instable salts; for metathetical reactions; and for oxidation and reduction cells. The result of the test has been so satisfactory that we have no hesitation in calculating chemical affinity from the equilibrium phenomena in cases where it is difficult or impossible to make the reaction take place in a voltaic cell. In that most useful reaction to physical chemists, the action of alcohol on acetic acid, we should be quite put to it to arrange that as a voltaic cell. It is a reaction for which the equilibrium can be measured and formulated. The van't Hoff formula gives us a method of calculating the chemical affinity for this reaction. In most cases we make use of the electrical method if possible, because it is usually simpler and more accurate. However, if there is any reason for doubting the accuracy of the electrical methods, we fall back at once on the method of the equilibrium constant. One instance of this is to be found in the hydrogen-oxygen gas cell. No one has ever observed experimentally an electromotive force of about 1.22 volts for the gas cell; but this is the value obtained from the chemical reactions which have been studied[1] and it is generally accepted as more accurate than the values obtained by direct measurement.

Since the strength of an acid is proportional to the concentration of ion, and since the concentration of hydrogen as ion at any dilution depends on the equilibrium (or dissociation) constant, it is customary to speak of this latter as the affinity constant of the acid. There is a certain confusion of ideas about this because, in the sense that we have been using the word, the equilibrium constant is a function of the chemical affinity only for the reaction $HX \rightleftarrows H^{\cdot} + X'$. It is in this sense that the word is used by van't Hoff.[2]

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[1] Nernst: Zeit. Elektrochemie, 11, 835 (1905); Lewis: Jour. Am. Chem. Soc., 28, 170 (1906).

[2] Zeit. phys. Chem., 3, 608 (1889).

While we can determine the chemical affinity whenever we have a reversible reaction which we can measure electrically or chemically, we are completely at a loss for the present with regard to reactions which are practically irreversible.[1] The inversion of cane sugar to dextrose and laevulose is a reaction running practically, if not theoretically, to an end. No one has ever succeeded in reversing it and we do not know where the equilibrium point is or even whether there is an equilibrium point. Consequently we cannot calculate the chemical affinity corresponding to this reaction. The reaction cannot be arranged as a voltaic cell. The oxidation of an alkaline pyrogallol solution is a reaction which can be studied electrometrically; but it is not reversible and therefore we cannot calculate the chemical affinity, though we may be able to assign a limiting value. To this extent we are better off than in the case of the sugar inversion where we have only a reaction velocity formula from which no conclusion can be drawn. If we are to get numerical values for the chemical affinity corresponding to apparently irreversible reactions, it seems that we should begin by making a careful study of irreversible oxidation and reduction cells. As long ago as 1892, I called attention to the fact[2] that there were two classes of reducing agents, those which formed an oxidizing agent when oxidized and those which did not. A similar distinction holds good in regard to the reduction of oxidizing agents. It would have been better to have distinguished oxidizing or reducing agents with which the reaction is readily reversible from those with which the reaction is practically irreversible; but the instances cited at the time made the meaning clear. Since then, most of the work has been on reversible oxidizing and reducing agents because the theory is simpler, but it seems to me that the time has come to take up the study of the irreversible class.

In paragraph 918 Faraday says "that the electric current is only another form of the force of chemical affinity," and

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[1] Cf., however, v. Wartenberg: Zeit. phys. Chem. 61, 366 (1907).

[2] Zeit. phys. Chem., 10, 407 (1892).

that "the forces termed chemical affinity and electricity are one and the same." Strictly speaking, the fact that chemical energy can be converted into electrical energy is not a proof that the two are the same thing. It is only by seeing how far such a hypothesis is a successful working one that we can tell what its limitations are or whether it has limitations.

8. Inter-relation of Chemical and Electrolytic Action.

The most striking characteristic of an electrolytic reaction is that it occurs in two places—at the anode and at the cathode.[1] 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 the cathode processes interfering and perhaps of one 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.

If we dissolve copper in sulphuric acid, the formation of copper sulphate is the anode reaction and the reduction of

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[1] Cf. Trans. Am. Electrochem. Soc., 9, 13 (1905).

[2] Traube: Ber. chem. Ges. Berlin, 26, 1473 (1893); Haber: Zeit. phys. Chem., 34, 513; 35, 81, 608 (1900); Zeit. Elektrochemie, 7, 411 (1901).

sulphuric acid is the cathode process. This same reaction takes place electrolytically even with a more dilute acid. In the directions for the electrolytic determination of copper[1] we read that "if the current be permitted to act too long in the presence of sulphuric acid, copper sulphide may be produced."

This identity of chemical reaction and electrolytic reaction has not always been admitted. Tafel[2] disputes it flatly, basing his conclusion on what seems, at first sight, to be conclusive evidence. The experiments were all made with a solution containing both nitric acid and sulphuric acid.

"Nitric acid in a sulphuric acid solution is reduced electrolytically almost exclusively to hydroxylamine when an amalgamated cathode is used which has a distinct electrolytical reducing action on hydroxylamine sulphate.

"On the other hand nitric acid is converted almost completely into ammonia in presence of a copper cathode which acts more slowly and with a lower current efficiency, in spite of the fact that the copper cathode is entirely unsuited for the further reduction of hydroxylamine sulphate when once formed.

"From these facts one is justified in drawing the conclusion that *hydroxylamine is not an intermediate stage in the reduction of nitric acid to ammonia at a copper cathode.*

"To account for this phenomenon one may make different hypotheses and, at first sight, it may seem the simplest assumption that the formation of hydroxylamine is a specific chemical action of the metals concerned. This is certainly not correct for mercury. It has long been known that in the presence of very concentrated sulphuric acid mercury reduces nitric acid readily to nitric oxide, and mercury is used in Lunge's nitrometer for the quantitative determination of nitric acid. That a more dilute acid acts in the same way and that not a trace of hydroxylamine is formed by the action of mercury on nitric acid has been proved by me in special experiments so

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[1] E. F. Smith: "Electro-Analysis," 4th Ed., 66.

[2] Zeit. anorg. Chemie, 31, 291 (1902).

contrived as to duplicate the conditions of electrolysis as closely as possible.

"On the other hand, the following hypothesis seems to me to account for all the facts and to have the further advantage of bringing these facts into line with Chilesotti's[1] views and experiments with regard to the effect of different cathodes on the reduction of nitrobenzene. Chilesotti concludes that, in the reduction of nitrobenzene to aniline in acid solution,[2] the specific electrolytic reduction leads only to the formation of phenylhydroxylamine and that the further reduction of this substance to aniline depends chiefly on the purely chemical action of the cathode or of the metals specially added to the cathode solution.

"The matter of the electrolytic reduction of nitric acid seems to me a little different, though analogous to a certain extent. From the facts already referred to, it is impossible to avoid drawing the conclusion that the electrolytic reduction of nitric acid in sulphuric acid solution proceeds with great energy [?] as far as the formation of hydroxylamine and that this solution is not easily reduced farther.

"Special experiments have proved conclusively that the change in the course of the reaction which takes place in the presence of certain metals, notably copper, and which leads straight to ammonia, is *not* due to a secondary chemical action of these metals on hydroxylamine previously formed. Hydroxylamine sulphate is quite stable in presence of copper, copper sponge or copper sulphate in acid solution. I assume therefore that certain cathode materials, such as copper, change the course of the reduction from the specific electrolytic path leading from nitric acid to hydroxylamine in such a way that the reaction does not proceed through the hydroxylamine stage at all, but passes it by and forms ammonia direct. I cannot yet say certainly at what stage of the

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[1] Zeit. Elektrochemie, 7, 768 (1901).

[2] Cf. the patents of the firm, C. F. Boehringer and Sons. D. R. P., 116942, 117007 (1899); also Elbs and Silbermann: Zeit. Elektrochemie, 7, 589 (1901).

reaction this change takes place but it seems to me not improbable that it occurs at that of dihydroxylamine, $NH(OH)_2$. The dihydroxylamine must be looked upon as corresponding to phenylhydroxylamine in the change from nitrobenzene to aniline.

$$\begin{array}{lll} C_6H_5.NO_2 & C_6H_5.NHOH & C_6H_5.NH_2 \\ OH.NO_2 & OH.NHOH & OH.NH_2 \end{array}$$

The product corresponding to aniline is not ammonia but hydroxylamine.

"By using a mercury cathode and graded cathode potentials I shall try to furnish an experimental proof for the correctness of this hypothesis.

"Through the investigation of the electrolysis of nitric acid in sulphuric acid solution conclusive proof has been furnished that the electrolytic reduction at a special cathode (copper, mercury) may differ *not only quantitatively*, but *qualitatively* from the chemical reducing action of the cathode metal in presence of an identical electrolyte. This seems to me a result of general importance.

"In addition we have the observation that two metals, copper and mercury, which give the same product, nitric oxide, by chemical action on a mixture of nitric and sulphuric acids, produce an entirely different result when used as cathodes, the first forming ammonia almost entirely and the second almost entirely hydroxylamine.

"One's right to speak of a *specific electrolytic* reducing action at a definite cathode in a definite solution cannot be disputed any more, even though this specific electrolytic action is often masked by other influences.

"I have advanced the hypothesis that the formation of hydroxylamine, in other words the reducing action at a mercury cathode, is to be looked upon as a specific electrolytic reduction of nitric acid in sulphuric acid solution and that this is interfered with by chemical action in the case of other cathodes, especially copper. Therefore the combination of electrolytic reduction and chemical disturbance leads directly to ammonia while electrolytic reduction alone leads first to hydroxylamine and afterwards only 'gradually to ammonia through 'over-reduction' at cathodes with especially high hydrogen polarization.

"At many cathodes, such as tin in hydrochloric acid solution, there may also be a direct chemical reduction of nitric acid to ammonia and hydroxylamine so that here the work of the current consists entirely or partly in reprecipitating the tin that has gone into solution. But it seems to me to have been established incontrovertibly by the preceding experiments that such a point of view[1] is not tenable for every electrolytic reduction at any cathode."

Further on in the same paper Tafel[2] describes experiments on the chemical action of copper, mercury, and lead on nitric acid in presence of sulphuric acid.

"The following experiments were carried out with the intention of learning whether perhaps the very different results of the electrolytic reduction of nitric acid with different cathodes might be referred to the chemical action of nitric acid on the metals in question. The experiments were therefore carried out as far as possible under the same conditions under which a possible chemical action of the metals on nitric acid must take place during [electrolytic] reduction. The experiments were therefore made in presence of a large amount of sulphuric acid, at ordinary temperature, with continuous shaking. Only in this way, at least with lead and mercury, could the conditions prevailing during electrolysis be maintained; for without vigorous shaking salts soon precipitate on the surface of the metal and prevent the further action of the nitric acid. If one assumes a possible chemical action of the metals during the electrolysis one may also make the assumption that the surface is kept in a state for the chemical reaction through continuous reprecipitation of the metal by the current.

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[1] For reasons which will be explained later, the fact that a reduction takes place more energetically at a definite cathode during electrolysis than with finely-divided metal without electrolysis, cannot be looked upon as a legitimate argument against such a conception.

[2] Zeit. anorg. Chem., 31, 309 (1902).

"This consideration vitiates all proofs as to the existence of a specific electrolytic reduction differing from the chemical action of an attackable cathode, so long as these proofs are based only on the fact that the reduction in question takes place more energetically during electrolysis than without it; for in so far as we are dealing with readily soluble salts, we must assume that the removal of these salts from the surface of the electrode by the current will have a very beneficial effect upon the reaction.

Copper, Nitric Acid and Sulphuric Acids

"I placed 10.1 grams of a thin clean piece of copper wire, cut in short pieces, in a round-bottomed flask holding about 150 cc and added 20 cc of a 50 percent sulphuric acid and 2 cc of a dilute nitric acid containing 1 gram HNO_3. After a few seconds there began a violent evolution of gas which however soon slacked up. The flask was then placed on a horizontally-acting shaking machine and connected by means of rubber stopper and rubber tubing with a Volhard apparatus containing a concentrated solution of iron vitriol. After a brief period of shaking the evolution of gas ceased and the solution appeared cloudy. On adding 20 cc of water and shaking some more, the evolution of gas increased and the iron vitriol solution became dark colored, owing to the absorption of large amounts of nitric oxide. After shaking for several hours the solution in the flask was turbid, due to the presence of crystallized copper sulphate, and the evolution of gas had ceased. A further addition of 20 cc water caused the evolution of gas to begin again. The undissolved copper weighed 8.54 grams and consequently 1.65 grams Cu had dissolved. The equation

$$2HNO_3 + 3Cu + 3H_2SO_4 = 3CuSO_4 + 2NO + H_2O$$

requires 1.52 grams copper for 1 gram HNO_3.

"The slight difference between experiment and theory is due in part to the fact that in this experiment air was not rigorously excluded from the flask. Every time the flask was opened some air passed in and colored the vapor phase brown with formation of nitrogen dioxide. On further shaking this was reduced with a corresponding consumption of copper.

"A portion of the solution containing copper sulphate was tested for hydroxylamine by adding Seignette salt and an excess of alkali. No hydroxylamine was formed.

"The remainder of the solution was treated with an excess of concentrated caustic potash and three-quarters of it distilled into a cooled Volhard apparatus containing water. After adding a few drops of methyl orange the distilled liquid required 0.14 cc tenth-normal hydrochloric acid to produce a red color. Just as much standard acid was needed when the same amount of a caustic potash solution was distilled by itself and the distillate titrated.

"By the action of copper on nitric acid in presence of sulphuric acid, neither ammonia nor hydroxylamine is formed in perceptible amounts.

Mercury, Nitric Acid and Sulphuric Acid

"If pure mercury is shaken with a solution of nitric acid in 50 cc sulphuric acid, it changes very quickly into a mass of little globules while brown fumes are given off and a white precipitate of mercurous sulphate is formed. There was shaken together 40 grams mercury, 20 cc 50 percent sulphuric acid and 2 cc dilute nitric acid containing 1 gram HNO_3 in a closed flask in a shaking machine. The flask was opened occasionally and at first a heavy pressure was noticed. After shaking for three hours the reaction was at an end. The filtrate from the mercury and the mercurous sulphate contained small amounts of nitrous acid[1] which were driven out by a short boiling. After that, a portion decolorized a small amount of potassium permanganate (for the whole amount of liquid 0.6 cc of a solution of which 1 cc corresponded to 1.6 mg hydroxylamine). But even this amount of reduction is not to be ascribed to hydroxylamine in the solution, as it is due to the presence of mercurous sulphate. A drop of hydrochloric acid produced a white precipitate in the solution and

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[1] Formed by action of the air on dissolved nitric oxide.

the filtrate from this was colored by the first drop of a very dilute potassium permanganate solution.

"Therefore hydroxylamine is not formed in measurable amounts during the chemical action of mercury on nitric acid under conditions approximating as closely as possible to those of my electrolytic experiments. That nitric oxide is formed has long been known. The same product is thus formed in both cases during the chemical reduction of nitric acid by copper and by mercury."

Experiments on the chemical action of lead on a mixture of nitric and sulphuric acids resulted chiefly in the formation of nitrous acid, the chemical action thus being different from that of either copper or mercury. In the electrolytic experiments a lead cathode gave more hydroxylamine than a copper one and less than a mercury one.

I have quoted from this paper of Tafel's at great length because we have here a series of carefully planned experiments which apparently prove conclusively that the electrolytic reduction is quite distinct in nature from the chemical reduction. As a matter of fact, this conclusion has been proved to be wrong as regards copper and is therefore probably wrong as regards mercury though this will have to be settled definitely by special experiments.

The matter of the copper in nitric acid has been cleared up by Turrentine[1] in my laboratory. 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. This is the point that was overlooked by Tafel and which vitiates all his conclusions in regard to copper and presumably all those in regard to mercury and lead. To show that this difference in conditions was the cause of the difference in the products, Turrentine electrolyzed

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[1] Jour. Phys. Chem., 10, 715 (1906).

a solution of copper nitrate and nitric acid 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 way 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, but Turrentine overcame the difficulty in another way. 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 of Turrentine's were performed to prove that the difference between the electrochemical and 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 conducting solutions. 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.

While the presence of ions of the cathode metal in solution is disadvantageous in the reduction of nitric acid to ammonia or hydroxylamine, this is not always the case. Indigotine is reduced to indigo white by zinc and alkali.

Here the dissolving of the zinc is the anode reaction and the reduction of the indigotine at a zinc cathode is the cathode reaction. We should, therefore, expect to find that indigotine could be reduced at a zinc cathode in an alkaline solution in presence of zinc salts. This has been shown experimentally by Binz[1] who found that little or no indigo white was obtained when there were no zinc salts in the cathode chamber. If the alkali had been concentrated enough to dissolve the zinc cathode readily, it would not have been necessary to have added zinc salts. This seems to be the case in the electrolytic reduction of nitrobenzene to aniline at a copper cathode in acid solution.[2] It was found that the reduction was equally successful whether one started with a copper cathode or with a platinum cathode and added copper salts to the solution. It is to be noticed that the direct action of copper on nitrobenzene produces aniline so that there is not the apparent discrepancy which was noted in the reduction of nitric acid.

The reduction of nitrates in neutral or alkaline solutions depends on the nature of the cathode.[3] With gold, platinum, lead or iron cathodes, the chief reduction product is ammonia. With spongy copper or spongy silver cathodes the chief reduction product is nitrite and this is also the case with amalgamated copper cathodes.[4] Müller and Weber[5] have shown that the chemical action of copper on nitrate produces nitrite and not ammonia while Hatton[6] has shown that spongy ion reduces nitrates chemically to ammonia. By measuring cathode potentials Müller and Spitzer[7] have shown that the chemical behavior runs parallel with the depolarization values. The depolarization values are not always entirely

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[1] Zeit. Elektrochemie, 5, 5, 103 (1898).

[2] Boehringer and Sons, D. R. P., 116942, 117007 (1899); Cf. Chilesotti: Zeit. Elektrochemie, 7, 768 (1901).

[3] Müller and Weber: Zeit. Elektrochemie, 9, 955 (1903); Müller and Spitzer: Ibid., 11, 509 (1905).

[4] W. J. Müller: Ibid., 9, 978 (1903).

[5] Ibid., 9, 965 (1903).

[6] Jour. Chem. Soc., 39, 27 (1881).

[7] Zeit. Elektrochemie, 11, 509 (1905).

trustworthy.[1] There may be catalytic actions due to the metals which may not show as a potential difference.[2] The one thing which will always hold true is that the chemical action and the electrolytic action will be identical provided the conditions are the same in the two cases. Foerster[3] has called attention to the parallelism between the chemical action and the cathode behavior of metals. Among other instances he cites the behavior of chloric acid which is readily decomposed by iron[4] and is also readily reduced electrolytically at an iron cathode.[5]

As regards the electrolytic reduction of nitric compounds I quote the remarks of Buchner[6] at the tenth annual meeting of the German Bunsen Society in Berlin.

"In my work on the electrolytic reduction of aromatic nitro compounds to the corresponding amines I started with the idea that when a metal reduced a nitro compound chemically and quantitatively to the corresponding amine, that metal must produce the same results under electrolytic conditions either as cathode or when added to the cathode because it would be carried into solution chemically and would be precipitated electrolytically by the current. As a matter of fact I was able to show experimentally that a whole series of metals kept their specific chemical action during electrolysis. Thus in acid solution one can reduce aromatic nitro compounds to the corresponding amines with iron, tin, lead and copper, either chemically or electrolytically. Similarly one can reduce aromatic nitro compounds in alkaline solution to hydrazo compounds chemically with tin, zinc, and lead while according to the Bayer patents the same reduction products can be obtained electrolytically with electrodes of these metals.

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[1] Müller: Zeit. anorg. Chem., 26, 1 (1901); Riss: Zeit. phys. Chem., 44, 641 (1904).

[2] Tafel: Zeit. Elektrochemie, 9, 645 (1903).

[3] Elektrochemie wässeriger Lösungen, 308.

[4] Hendrickson: Am. Chem. Jour., 32, 242 (1904)

[5] Foerster: Zeit. Elektrochemie, 4, 386 (1898).

[6] Ibid., 9, 646 (1903).

"From my point of view excess voltages and catalytic actions are of much less importance in these cases than the specific chemical effects. The matter is entirely different, however, in my experiments on the electrolytic reduction of aromatic nitro compounds to the corresponding amines in alkaline solution with a copper cathode. Here it is not possible to speak of a purely chemical action and I rather favor the view that we are dealing with a catalytic action of copper. Copper can scarcely be detected chemically in the solution while in the other cases of the acid solution salts of the cathode metal were always present in the electrolyte. Thus in the reduction of nitrobenzene in hydrochloric acid solution with a copper cathode, a double salt with the amine is present in the solution if the current is not allowed to run too long."

Personally I should not make the distinction into two classes as Buchner does. There are enough experiments with metals in strongly acid or strongly alkaline solutions to show that the reduction of nitrobenzene to aniline at a copper cathode is what would take place as the cathode reaction if copper were to dissolve in caustic soda with an evolution of hydrogen. The chemical method, as I have said before, is less flexible than the electrochemical method in conducting solutions; but that does not involve any new principle. If one is to distinguish two classes at all, they must correspond to the reduction of nitric acid at a copper cathode in the presence or absence of a copper salt. While we do not know to what the so-called "excess voltage" is due, its effect appears in the same way both in the chemical and the electrolytic experiments.

The instances of the identity between chemical and electrolytic reactions have been taken so far from the cathode reactions. We can find a number of interesting cases among the anode reactions, illustrating the same point. The oxidation of chromic sulphate to chromic acid takes place more readily at lead peroxide anodes than at those of platinum[1]

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[1] Regelsberger: Zeit. Elektrochemie, 6, 308 (1899. Le Blanc: Ibid., 7, 292 (1900). Müller and Soller: Ibid., 863 (1905)

and lead peroxide oxidizes chromic sulphate to chromic acid. The electrolytic formation of periodate at a lead peroxide anode is merely an electrolytic duplication of the chemical reaction.[1] Kempf[2] states that in dilute sulphuric acid solution lead peroxide oxidizes benzene to quinone and that this reaction can be carried out electrolytically by using lead anodes. Sebor[3] finds that *p*-toluene sulphonic acid is scarcely oxidized at all at a platinum anode while it is readily oxidized at a lead cathode. No explanation for this phenomenon was offered by him, but there seems no reason to suppose that this case is different in any way from the preceding three. The oxidation of ammonia to nitrites takes place in alkaline solutions in presence of oxygen and copper or cupric hydroxide. This has been duplicated electrolytically by Tafel and Biltz.[4]

Löb[5] has shown that dimethylaniline can be oxidized at platinum anodes to tetramethyl benzidine provided chromic acid is added to the solution and that this is merely an electrolytic duplication of the chemical oxidation. The firm of Boehringer and Sons[6] has made use of manganese salts as catalytic agents in electrolytic oxidation and has shown that these salts act chemically after having been converted electrolytically into manganic salts or permanganates as the case may be. White[7] has extended the work of Lorenz[8] on ferromanganese anodes and has shown that the electrolytic and chemical phenomena run parallel throughout. Walker[9] has shown that the rusting of iron is essentially an electrolytic phenomenon and Curry[10] has shown that the chemical and the electrolytic corrosions are the same in the case of the bronzes.

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[1] Müller: Zeit Elektrochemie., 10, 49 (1904).

[2] Ibid., 7, 592 (1901).

[3] Ibid., 9, 370 (1903).

[4] Ber. chem. Ges. Berlin, 37, 3130 (1904). Cf. Müller and Spitzer: Ibid., 38, 779 (1905).

[5] Löb: Zeit. Elektrochemie, 7, 603 (1901).

[6] Ibid., 7, 625 (1901); 8, 219 (1902).

[7] Jour. Phys. Chem., 10, 502 (1906).

[8] Zeit. anorg. Chem., 12, 393 (1896).

[9] Jour. Am. Chem. Soc., 29, 1251 (1907).

[10] Jour. Phys. Chem., 10, 474 (1906).

The behavior of cobalt salts in preventing the formation of hypochlorites[1] is known to be due to the chemical action of the cobalt salt on the hypochlorite, oxygen being set free and the cobalt salt oxidized to cobaltic hydroxide. At ordinary temperatures the effect ceases as soon as all the cobaltous salt has been oxidized to cobaltic salt. It has been said that this becomes a true case of catalysis at higher temperatures; but this point calls for further study.

The data at hand do not seem to warrant any definite conclusion as to the cause of the catalytic action of chlorides, chlorates, sulphates and fluorides on the formation of periodates[2] or of chlorides[3] or fluorides on the formation of persulphates.[4] We get an "excess voltage" at the anode[5] corresponding in some respects to that at the cathode. The analogy is probably closer than it seems at first sight because a cadmium salt in solution raises the voltage at which hydrogen precipitates at a platinum cathode. When we can explain either set of phenomena, we shall probably be able to explain the other. With the fluoride it seems quite certain that there is some relation between the greater oxidizing effect in fluoride solutions and the formation of ozone when fluorine acts on water.

While we are somewhat at a loss in this case, it is a pleasure to note that Foerster[6] calls attention to the fact that the somewhat complicated reaction in the electrolytic formation of perchlorate from chlorate is precisely the same as the chemical reaction.

In a previous paper[7] I have pointed out that the electrolytic deposition of metals from solutions follows the general

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[1] Oettel: Zeit. Elektrochemie, 5, 3 (1898).

[2] Müller: Ibid., 10, 64, 753 (1904). Cf. Skirrow: Zeit. anorg. Chem., 33, 25. Levi: Zeit. Elektrochemie, 12, 433 (1906).

[3] Elbs and Schönherr: Zeit. Elektrochemie, 2, 250 (1895).

[4] Müller: Ibid., 10, 776 (1904); 13, 681 (1907).

[5] It is quite possible that the effect of manganese salts on electrolytic oxidation may be due to the same cause.

[6] Elektrochemie wässeriger Lösungen, 490. Cf. Oechsli: Zeit. Elektrochemie, 9, 807 (1903).

[7] Jour. Phys. Chem., 9, 277 (1905); 12, 36 (1908).

laws of chemical crystallization and that the conditions favoring the production of large crystals by chemical methods are also those which give rise to a relatively coarse crystallization when a metal is precipitated electrolytically.

When we come to cases of apparently abnormal electrolysis, a knowledge of the chemical reactions involved helps us out. These reactions were first studied by Luther.[1] With an alkaline methyl alcohol solution containing a gold salt he obtained gold at the anode. What happens is that the alcohol is oxidized to aldehyde which then reduces the gold salt. With concentrated sodium carbonate and either permanganate or gold, we have a reduction to manganate or to metallic gold as the case may be. Here the intermediate stages are percarbonate and hydrogen peroxide, this last being the actual reducing agent. With sulphuric acid and permanganate there is also a reduction at the anode, due to the formation of persulphuric acid and of hydrogen peroxide. With a slightly acid nitrate solution to which potassium iodide has been added, iodine is obtained at the cathode. The current reduces nitric acid to nitrous acid and this last oxidizes the iodide to iodine. Kaufmann[2] has shown that an iron cathode dissolves in ammonium nitrate solution. This is because the current forms an ammoniacal ammonium nitrate solution which in itself dissolves iron. A much more remarkable case is that discovered by Kraus[3] that lead dissolves at the cathode and precipitates at the anode during the electrolysis of a solution of $NaPb_2$ in liquid ammonia between lead electrodes. This seems to be due to the existence of Pb_2' as an univalent anion in liquid ammonia. Tafel[4] reports the dissolving of mercury cathodes when methyl ethyl ketone is electrolyzed in acid solution. Beetz[5] has observed the evolution of hydrogen at a magnesium

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[1] Zeit. Elektrochemie, 8, 647 (1902).

[2] Ibid., 7, 733 (1901).

[3] Jour. Am. Chem. Soc., 29, 1563 (1907).

[4] Ber. chem. Ges. Berlin, 39, 3626 (1906).

[5] Phil. Mag. [4] 32, 269 (1866).

anode, but this needs confirmation because it may be merely a case of disintegration of the anode. V. Meyer[1] found that hydrogen acts on acidified permanganate solutions with evolution of oxygen. It follows from this that oxygen must be evolved at the cathode if one reduces acidified permanganate electrolytically. This prediction has been verified experimentally in my laboratory by Mr. Turrentine. Work is now being done to determine the nature of the reaction involved. Tommasi[2] reports that both hydrogen and chlorine are set free at the cathode when chloral hydrate is reduced electrolytically. The reaction has not been studied further, so that it is impossible to say just what happens. There is no reason to suppose however that the explanation will be hard to find.

What seems to be a different type of case has just been discovered by Wood and Jones.[3] On electrolyzing a double carbonate of copper and potassium, metallic copper was precipitated at both electrodes. So far as one can judge from the meagre details this seems to be a case of a complex anion breaking down and precipitating copper. This in itself does not seem very probable and one cannot help wondering whether the anode precipitate might not have been cuprous oxide as we know that it is in the electrolysis of Fehling's solution.[4] The possibility of an intermediate formation of percarbonate should also be considered. That would make this case like Luther's experiment with sodium carbonate and a gold salt.

III. ELECTROLYSIS IN NON-CONDUCTING SOLUTIONS

While there is nothing about reactions in conducting solutions which is inconsistent with Faraday's conception of the equivalence and possible identity of chemical affinity and electrolysis, the case is very different when we come to reactions in organic solvents. The theory of Berzelius shat-

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[1] Ber. chem. Ges. Berlin, 29, 2549, 2828 (1906).

[2] Elektrochemie, 741.

[3] Proc. Camb. Phil. Soc., 14, 171 (1907).

[4] Luther: Zeit. Elektrochemie, 8, 649 (1902).

tered against the facts of organic chemistry and these same facts have checked the development of the theory of Faraday and Helmholtz. It is therefore only by a study of the facts of organic chemistry that we can settle to what extent the theory of Faraday is a good working hypothesis. In the remainder of this too long paper, I intend to point out how the problem is to be attacked. Some preliminary experiments are already under way in my laboratory and I hope that others will be interested enough in the problem to attack it themselves.

Under direct electrical methods we have the high frequency discharge, the silent discharge, and direct electrolysis. The silent discharge may be simply a light phenomenon, as we know it to be in the formation of ozone. If so, it should not be classified under the electrical methods. The method has not given the results which it should. This has been due in part to the essentially qualitative nature of the researches thus far carried out and in part to the fact that alternating current has been used instead of direct current.[1] The high frequency discharge has yielded some very interesting results[2] and it is to be hoped that Messrs. Jackson and Laurie will continue these very promising investigations. Direct electrolysis is possible in some few cases; but its application is extremely limited practically. Of course we can claim that it is only the lack of time at our disposal which hinders us. In one of the passages previously quoted, Helmholtz has stated this clearly.[3] "In order to produce a current of sufficient strength to collect enough of the products of decomposition without producing too much heat in the electrolyte, the substance which we try to decompose ought not to offer too much resistance to the current. But this resistance may be great, and the motion of the ions may be very slow, so slow indeed that we should need to allow it to go on for hundreds of years before we should be able to collect

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[1] Trans. Am. Electrochem. Soc., 9, 20 (1906).

[2] Jackson and Laurie: Proc. Chem. Soc., 22, 155 (1906).

[3] Helmholtz: Jour. Chem. Soc., 39, 291 (1881).

even traces of the products of decomposition; nevertheless all the essential attributes of the process of electrolysis could subsist." Such an argument is entirely satisfactory for the use which Helmholtz makes of it, namely, to show that the theory of Faraday is not necessarily inconsistent with the phenomena of organic chemistry. On the other hand it is of no account as a means of proving that Faraday's theory does represent the facts. To test this latter question we must devise what I have called rapid methods of electrolysis in non-conducting solutions.

The line of argument is similar to that in which it was shown that chemical affinity could be calculated from the van't Hoff formula. Chemical affinity as calculated from the equilibrium relations was found to be equal to that calculated from electromotive force measurements in all cases where the two were comparable. We therefore conclude that the equilibrium relations enable us to calculate what would be the electromotive force which a cell would have if it could be so constructed as to give us the ester formation, for instance. If we can now show that certain non-electrical methods give the same results as electrolysis in all cases in which a comparison is possible, we are justified in concluding that these same non-electrical methods will give results in other cases which are identical with those which we should get if the solution conducted sufficiently well to make electrolysis practicable.

First among these methods comes the Gladstone and Tribe zinc-copper couple.[1] The couple reduces a potassium nitrate solution first chiefly to nitrite and then to ammonia if experiments are made at ordinary temperature.[2] This is exactly what was found by Müller and Spitzer[3] for electrolytic reduction with a copper cathode. Working in hot solutions Thorpe[4] was able to develop a quantitative method

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[1] Proc. Roy. Soc., 20, 218; Jour. Chem. Soc., 25, 461 (1872).

[2] Gladstone and Tribe: Jour. Chem. Soc., 33, 140 (1878).

[3] Zeit. Elektrochemie, 11, 509 (1905).

[4] Jour. Chem. Soc., 26, 541 (1873).

for determining nitrites as ammonia. The object of heating the solutions was to accelerate the reaction; and we know that at silver cathodes raising the temperature is unfavorable to the nitrite formation[1] but it is not fair to assume that the effect would be more marked in the case of copper cathodes under similar conditions.[2] It is interesting to note Thorpe's experience with ammonium nitrate.[3]

"Of all the nitrates experimented upon, the most difficult of reduction appears to be *ammonium nitrate*. From the irregularity of the results obtained, I was inclined to believe that the decomposition was incomplete, or that hydroxylamine might be formed, or possibly Divers' hyponitrous acid. Direct experiments, however, have failed to point out the formation of these substances. The discordances appear to depend upon differences in the strength of the solution and the amounts of zinc and copper taken. If the solution is too strong, nitrogen dioxide is evolved, and if the amount of zinc and copper be insufficient the reduction is incomplete."

In view of what we know as to the solvent action of an ammonium nitrate solution on copper, it is probable that the case is similar to that of reduction in an acid solution in presence of a copper salt. This is confirmed by the experiments of Gladstone and Tribe.[4]

The zinc-copper couple reduces a hot solution of potassium chlorate to chloride[5] and the same result was obtained electrolytically by Burrows[6] working with copper electrodes. The couple reduces nitrobenzene to aniline[7] and we have already seen that this same reduction takes place electrolytically at a copper cathode.[8] The couple reduces indigo-blue

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[1] Müller and Spitzer: Zeit. Elektrochemie, 11, 513 (1905).

[2] Cf. C. F. Boehringer and Söhne: Zeit Elektrochemie, 12, 745 (1906)

[3] Jour. Chem. Soc., 26, 544 (1873).

[4] Ibid., 33, 151 (1878).

[5] Thorpe: Ibid., 26, 547 (1873). Eccles: Ibid., 29, 856 (1876). Gladstone and Tribe: Ibid., 33, 147 (1878).

[6] Jour. Phys. Chem., 6, 417 (1902); 7, 537 (1903).

[7] Gladstone and Tribe: Jour. Chem. Soc., 33, 312 (1878).

[8] Chilesotti: Zeit. Elektrochemie, 7, 768 (1901).

to indigo-white in an alkaline solution, and Binz[1] has shown that the same reduction takes place electrolytically at a zinc cathode with a zinc salt in solution. Unquestionably the same result could be obtained with a zinc salt in solution and a copper cathode. The couple reduces arsenious acid to arseniuretted hydrogen. The same reaction takes place in the Marsh test with zinc in an acid solution, in other words at a zinc cathode. I do not know of any experiments with a copper cathode but I think there can be no question as to what the result would be.

These cases illustrate the identity between the action of the couple and that of the electrolytic cell. We now come to some intermediate cases. At 50° the couple reacts with chloroform dissolved in absolute alcohol, forming chiefly methane and zinc chloro-ethylate.[2] Small amounts of acetylene are also formed, the ratio of acetylene to methane increasing as we change from chloroform to bromoform and then to iodoform. Zinc foil alone does not react so rapidly or at so low a temperature as the couple but the final products are the same except so far as some acetylene may be retained by the copper. A solution of chloroform in absolute alcohol practically does not conduct at all; but some experiments made in my laboratory some years ago showed that chloroform could be decomposed electrolytically in alcoholic solution between zinc electrodes. Under these conditions it is not worth while to attempt much in the way of quantitative electrolysis. Fortunately, Gladstone and Tribe have tried some experiments with alcohol containing up to 25 percent of water. Oxychloride of zinc is formed instead of zinc chloro-ethylate; but that seems to be the chief difference. The gaseous product is almost entirely methane as before. Experiments are now being made in my laboratory on the electrolysis of these solutions. While the work is not yet finished, it has been established that chloroform is decomposed and

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[1] Zeit. Elektrochemie, 5, 5, 103 (1898).

[2] Gladstone and Tribe: Proc. Roy. Soc., 20, 218 (1872); Jour. Chem. Soc., 33, 508 (1875).

that methane is formed. The quantitative details will be given later.

Since the chief gaseous product is methane whether we work with chloroform in absolute alcohol or in aqueous alcohol, and since the electrolysis of the solutions in aqueous alcohol gives results paralleling those with the couple in the same solutions, we are justified in concluding that electrolysis in the absolute alcohol solution, would merely duplicate the results obtained by Gladstone and Tribe. There is however no obvious reason why we should differentiate between the decomposition of chloroform, bromoform or iodoform by the couple on the one hand and the decomposition of methyl or ethyl iodide[1] on the other hand. No solvent was used and the couple was added direct to the methyl iodide. The reaction is slow at ordinary temperatures and the first product is zinc methiodide which breaks down readily into zinc methyl and zinc iodide. The system does not conduct to any appreciable extent so far as we know; but we are undoubtedly getting the products which we should get if we could electrolyze methyl iodide between zinc electrodes. The following passage shows what Gladstone and Tribe[2] themselves thought about their couple.

"We have not hesitated in our papers to call the agent which we employ 'the copper-zinc couple,' although aware that this has frequently led to misapprehension. The term suggests to many minds the metallic elements of a voltaic battery; and the first impression conveyed has frequently been that we were using a battery of low intensity with its conducting wires, etc. We have, however, purposely retained the term because we have all along believed that the action was really of the same character as that which takes place in ordinary electrolysis, and indeed was identical with what occurs within the voltaic cell. There are two metals in contact, standing in the decomposable liquid, only instead of one

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[1] Gladstone and Tribe: Jour. Chem. Soc., 35, 10,556 (1879). Cf. Lachmann: Am. Chem. Jour. 19, 410 (1897).

[2] Jour. Chem. Soc., 35, 571 (1879).

pair of plates, or several pairs joined together, we have minute pieces of metal, forming myriads of circuits. There is this great advantage also in our arrangement, that the resistance of the binary compound is reduced to a minimum as it washes the very points of contact of the metals."

If we call the Gladstone and Tribe zinc-copper couple the first of our methods of performing electrolysis in non-conducting solutions, the second method should be called the chemical production of ions.[1] When sodium persulphate or persulphuric acid breaks down in aqueous solution we get the setting free of the sulphate ions. We should therefore expect to get the characteristic reactions of the sulphate ion, and we actually get just that. In an aqueous solution of persulphuric acid, either by itself or in contact with platinum, oxygen is evolved, the reaction being improved from a spectacular point of view by addition of a little manganous sulphate. When a strip of copper is placed in a sodium persulphate solution the amount of persulphate decomposed in any period of time is exactly equivalent[2] to the amount of copper changed into copper sulphate. This is as it should be because copper dissolves practically quantitatively when made anode in a sulphate solution. On the other hand nickel and aluminum do not dissolve to any great extent when made anodes in sulphate solutions and they are therefore not corroded by a sodium persulphate solution. Of course it might be urged that this chemical reaction is not strictly parallel to the electrolytic action, because we have the preliminary breaking up of the persulphate ion, S_2O_8'', which might introduce unknown complications. While I do not admit the validity of this hypothetical objection, there is another way in which we can duplicate chemically the action of electrolysis of sulphate solutions. Cobaltic sulphate breaks down spontaneously on gentle heating and sets free sulphate as ion. Ordinarily this is accomplished by the setting free of oxygen and the formation of sulphuric acid just as in the case

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[1] Cf. Trans. Am. Electrochem. Soc., 8, 43 (1905).

[2] Turrentine: Jour. Phys. Chem., 11, 623 (1907).

of electrolysis. Since the relatively stable ferric sulphate reacts with copper there can be no doubt that the instable cobaltic sulphate would do the same. Now if we were to allow some organic liquid to react with dry sodium persulphate which we can get or with anhydrous cobaltic sulphate which probably we cannot get, we could certainly speak of electrolysis in a non-conducting solution if our reaction product were to be a sulphonic acid for instance. I am not familiar with any experiments along this line with sulphates; but we get a parallel case with lead tetrachloride and Polis[1] states that chlorbenzene is formed when lead tetrachloride reacts with benzene. The weak point in this is that Polis did not start with lead tetrachloride and benzene. He started with lead tetraphenyl and hydrochloric acid, postulating the intermediate formation of the other pair of compounds.

Some experiments that we have made point to the fact that Polis was probably right in his conclusions though his method of reaching them may not have been orthodox. This is not an isolated case. In cobaltic sulphate we had a salt which broke down of its own accord because the metal radical changed valency. In ferric sulphate we have a substance which does not break down spontaneously into ferrous salt; but the valency of the metal radical can vary and we get the same reaction between copper and ferrous sulphate as between copper and cobaltic sulphate. In lead tetrachloride we have a basic radical with a varying valence and a compound which breaks down very easily. With benzene, lead tetrachloride acts as a halogen carrier substituting chlorine in the ring. The halogen carriers in actual use contain a basic radical with a varying valence. Though they are comparatively stable by themselves, they react with benzene substituting chlorine in the ring. The analogy is a bit striking and brings us very close to a working theory of halogen carriers. I shall not develop this further now because it belongs properly in a later paper on the electrochemistry of light.

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[1] Ber. chem. Ges. Berlin., 20, 716 (1887).

The percarbonates stand in the same relation to carbonates as the persulphates to sulphates. Addition of potassium cyanide or potassium iodide to copper sulphate solution sets free cyanogen or iodine respectively. These methods have found no application so far in organic chemistry. On the other hand Mulliken[1] has shown that the same new ester is formed whether we electrolyze sodium malonic ester or whether we add iodine to the solution.

The many reductions with zinc dust, with aluminum amalgam or with sodium amalgam, are all essentially cases of electrolysis in a non-conducting solution. They are to be classified as cases intermediate between the zinc-copper couple and the chemical production of ions.

As still a third method we have the action of light. If we adopt the theory of Grotthuss,[2] and look upon a ray of light as equivalent to a voltaic cell, the chemical actions of light become really electrochemical actions and we have found another very useful method of doing electrolysis in non-conducting solutions. Work is now being carried on in my laboratory to prove the correctness and usefulness of this theory of Grotthuss, so I will only call attention to the large number of reactions which will be included under this head if we succeed in establishing the validity and applicability of the theory of Grotthuss.

IV. SUMMARY

A necessary prerequisite to the general application of some modification of the theories of Berzelius and of Faraday is the proof of the existence of a polar state in organic compounds. The issue is clearly joined between Nernst[3] who believes in a non-polar union and Abegg[4] who upholds the polar view. Incidentally, any one upholding a polar theory must put forward some fairly definite hypothesis as to the

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[1] Am. Chem. Jour., 15, 523 (1893).

[2] Ostwald's Klassiker, 152, 115.

[3] Zeit. Elektrochemie, 7, 1005 (1901).

[4] Zeit. anorg. Chem., 39, 374 (1904).

conditions under which a definite element or a definite group can change from being positively polar to being negatively polar. In the reaction between zinc and methyl iodide for instance, the zinc is certainly positive in the compounds, zinc methiodide, zinc methyl and zinc iodide, while methyl and iodine are the negative radicals. In methyl iodide however the methyl group is presumably positive. Until we can tell something more definite about the conditions for the change of polarity, none of the conclusions drawn by Abegg are really binding. Take the case of iodine monochloride for instance. This reacts with caustic potash to form potassium chloride and hypoiodite. Abegg therefore considers iodine as positive and chlorine as negative. In HIO, however, the ions are $H^{\cdot}$ and IO' instead of $I^{\cdot}$ and OH'. We know that there has been a re-arrangement here and it seems difficult to prove that no other re-arrangements have taken place. It is conceivable that potassium iodide and hypochlorous acid were an intermediate step. In that case our conclusions would be reversed. As another instance, take the reaction between chlorine and benzene. It is certainly simpler to say that the positive chlorine replaces the positive hydrogen and that the negative chlorine unites with the positive hydrogen to form hydrochloric acid. In chlorbenzene, however, it would be natural to consider chlorine as negative and the phenyl radical as positive. In that case we should say that the negative chlorine replaced the negative hydrogen and that the positive chlorine combined with the negative hydrogen to form hydrochloric acid, in which there was afterwards a rearrangement such that the hydrogen becomes positive and the chlorine negative. This does not seem so attractive a way of putting it as the first one; but there is no way at present of proving that it is wrong. When hydrogen is set free electrolytically, we must assume a rearrangement if we are to consider hydrogen gas as polar. Another difficulty occurs in the case of monatomic sodium vapor. We cannot postulate a molecular compound as in the case of hydrogen or chlorine. A solution is possibly to be found in Nernst's theory of the chemical nature of electricity.[1]

All these difficulties are swept away at one stroke by Nernst's assumption of non-polar compounds. This would be a great relief if it were not that we introduce new complications. According to Nernst hydrochloric acid is a polar compound and ethyl chloride is not; but if we keep away from conducting solutions there seems to be no just reason for differentiating between hydrochloric acid and ethyl chloride. The existence of a definite polar compound[2] $NaPb_2$ is also a serious matter from the Nernst point of view. More serious still, is the fact that Nernst's view practically excludes all the possibilities to which I have called attention under the heading of electrolysis in non-conducting solutions. If the action of the Gladstone and Tribe couple on chloroform or methyl iodide is truly an electrolysis, it is difficult to see how there can be anything more than a qualitative difference between organic and inorganic compounds. Nernst's treatment of organic reducing agents and oxidizing agents[3] in terms of the hydrogen and oxygen electrodes respectively is inconsistent with his other position, and we are forced to conclude that the conception of organic substances as polar compounds is likely to prove fruitful experimentally.

If we grant the existence of polarity for the sake of argument, we come next to the extent of the subdivision. With potassium chloride we recognize only two ions, potassium and chlorine; but how about potassium nitrate? We can reduce it at the cathode to nitrite and it is therefore an oxidizing agent capable of setting up a definite oxygen concentration at a platinum electrode. Nernst's point of view in regard to oxidizing agents has proved a useful one and if

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[1] Nernst: Zeit. Elektrochemie, 7, 1005 (1901).

[2] It is interesting to note that lead tetraphenyl is made by the action of $NaPb_2$ on chlorbenzene, by the substitution of negative lead for negative chlorine. *One is tempted to predict that tin will be anion when sodium and tin are disolved in liquid ammonia.*

[3] Nernst and Lessing: Cf. Foerster, Elektrochemie wässeriger Lösungen, 127.

we adopt it, we must postulate some such reversible dissociation as that given by the equation

$$\mathrm{NO_3'} \rightleftarrows \mathrm{NO_2'^{\cdot\cdot}} + \mathrm{O''}.$$

This is merely the Berzelius theory over again and the only question is where we are to stop. There is still reduction to nitric oxide to be accounted for. It is not merely a question of organic chemistry. The electrolytic reduction of the nitrates, the nitrites, the chlorates, the sulphates,[1] etc., brings us face to face with the dilemma. Either we must apply some form of the Berzelius theory to these cases or we must revise all our present theoretical views in regard to electrolytic reduction and oxidation. There can be very little doubt as to what the answer will be to this. Since there is no experimental justification for distinguishing fundamentally between the reduction of nitrates and nitrobenzene, we come back again to the probable application of the Berzelius theory in some form to organic compounds.

The general results of this paper may be summed up as follows:

(1) Electrolytic and chemical actions are identical when carried on under the same conditions.

(2) The so-called "excess voltage" phenomena at metallic cathodes are duplicated when these metals are attacked chemically.

(3) Electrolysis in non-conducting solutions can be carried on with the zinc-copper couple; with sodium amalgam, aluminum amalgam, zinc dust, etc.; by chemical production of ions; and by means of light.

(4) Nernst's theory of non-polar compounds in the case of hydrogen, chlorine and the carbon compounds is inconsistent with his theory of oxidizing and reducing agents.

(5) The evidence is in favor of the general applicability of some modification of the dualistic theory of Berzelius.

(6) The evidence is in favor of the general applicability

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[1] Abegg: Zeit. anorg. Chem., 39, 374 (1904).

of some modification of Faraday's theory in regard to chemical affinity and electricity.

(7) We are handicapped by the lack of a definite theory as to the conditions under which a change of polarity takes place.

(8) It is possible that Nernst's theory of the chemical nature of electricity may be developed so as to help out on the question of reversible polarity.

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NEW BOOKS

Technische Anwendungen der physikalischen Chemie. *By Kurt Arndt. 14 × 22 cm; pp. vii + 304. Berlin: Mayer and Müller, 1907.*—In the preface the author says that in the last few years many physical chemical investigations have been carried out which have been of distinct, sometimes of great importance to the industries. This book contains an account of the most important results. One must keep in his mind or one will be disappointed in the book. Strictly speaking, "The Physical Chemistry of Technical Processes" would have been a more appropriate title than "Technical Applications of Physical Chemistry." The commercial manufacture of nitric acid from atmospheric nitrogen, of sulphuric acid by the contact process, of soda by the Solvay process, of iron in the blast-furnace, and of ozone has not been modified or helped appreciably by anything taken from physical chemistry, but these processes have been fruitful subjects of study by the physical chemists. Some day, of course, we shall point with pride to the things that physical chemists have done, but for the time being we are rather limited to the things that they might have done.

The first chapter is devoted to the formation of nitric oxide from the air and the author discusses in detail the experiments of Nernst and his pupils on the equilibrium involved. While it is assumed that the equilibrium is a question of temperature only, reference is made to the results obtained by Warburg and Leithäusser with the silent discharge. On the technical side, a brief account is given of the works at Notodden.

The second chapter deals with producer gas, furnace gas and water gas. The author takes up the equilibrium between carbon, carbon monoxide and carbon dioxide; the equilibrium in the blast-furnace; the dissociation of water vapor; and the water gas equilibrium.

In the third chapter the subjects are contact sulphuric acid, ammonia, and ozone. The part on sulphuric acid is admirable; that on ammonia is necessarily very short and consists chiefly of an account of Haber's work. Under ozone we have the work of Nernst and Clement, that of Fischer, and that of Warburg. The author does not bring out clearly the effect of different wave-lengths and apparently is not familiar with the work of Regener.

Catalytic agents form the subject of chapter four. A catalytic agent is defined as a substance which changes the rate of a chemical reaction without appearing among the final products of the reaction. This definition is well enough in its way; but the author precedes it by the statement that a catalytic agent cannot displace the equilibrium. Even in the case of a reversible reaction, equilibrium may be displaced by a solvent or by light. If we have a reaction which does not take place to any measurable extent in the gas phase, but which does take place in or at the surface of a catalytic agent, we shall get the equilibrium corresponding to that catalytic agent acting as a solvent, which may be and often is quite different from that occurring with another catalytic agent. One instance of this is to be found in the different action of heated surfaces on alcohol vapor.

The author believes that all catalytic actions depend on the intermediate formation of some compound or other. As instances of this, he cites the formation of ethyl sulphuric acid in the manufacture of ether, of nitrosyl sulphuric acid in the lead chamber process, of ferric sulphate in the contact sulphuric acid process with ferric oxide as catalytic agent, of platinum oxide in catalyses with platinum, etc., etc. Nearly ten pages are devoted to automatic platinum gas lighters.

The chapters on vaporization and condensation, on fusion and solidification, on polymorphous solids, on solutions, and on alloys have very little to do with technical processes, especially since the commercial methods of fractional distillation were worked out quite independently of any scientific knowledge of the subject.

Under solutions of several salts we have van 't Hoff's work on the Stassfurt deposits and here some improvements in the methods have actually been introduced as a result of van 't Hoff's investigations.

The eleventh chapter is devoted to colloidal solutions, the subheads being reversible and irreversible hydrosols; colloidal metals; colloidal gold solutions; colloidal silver; organic sols by Svedberg's method; the ultra-microscope; size of gold particles; ruby glass; dye-stuffs; filtration of colloids; precipitation of colloids by electrolytes; tungsten lamps; diffusion of carbonic acid through rubber. The squirting of carbon filaments might well have been mentioned here, since it is much more important for the moment than the tungsten lamp.

Decomposition pressures are the subject of the twelfth chapter while in the last chapter we have a brief account of the measurement of high temperatures. Altogether, this is a very readable book. *Wilder D. Bancroft*

Vorträge für Ärzte über physikalische Chemie. *By Ernst Cohen. Zweite, vermehrte und verbesserte Auflage. 16 × 24 cm; pp. viii + 264. Leipzig: Wilhelm Engelmann, 1907. Price: paper, 8 marks; bound, 9 marks.*—The general arrangement of the book is the same as in the first edition (5, 657); even the number of pages has changed but slightly. The only difference is that the book has been brought up to date. It was a valuable book when it first appeared and it is more valuable now. Practically everything that was said of it in the first review can be repeated now. It is true that there has been a change in the status of the electrolytic dissociation theory. We know now that we cannot determine molecular weights or percentage dissociations accurately in any except the most dilute solutions. This is, however, of very slight importance as yet in the biological applications since practically all of these involve qualitative relations only.

There is one qualitative application which might well be made in a future edition. The author states, p. 198, that sodium chloride increases the disinfecting power of a phenol solution while addition of glycerol decreases the toxic action of such a solution. It seems probable that this is merely a case of changing solubility. Sodium chloride decreases the solubility of phenol in water, increases its partial pressure and therefore its chemical potential, its effective concentration and its disinfecting power. Glycerol increases the miscibility of phenol with water and, in so far, decreases its toxic power. Of course this may not be the sole effect. We know that reaction velocities vary with the solvent, and therefore a partial change of solvent might easily change the rate at which phenol attacks animal membranes. This is, however, another factor and its possible existence should not prevent us from recognizing the effect due to solubility. *Wilder D. Bancroft*

Lehrbuch der theoretischen Elektrochemie auf thermodynamischer Grundlage. *By J. J. van Laar. 16 × 24 cm; pp. xii + 307. Amsterdam: S. L. van Looy (Leipzig: Wilhelm Engelmann), 1907. Price: paper, 6 marks; bound, 7.20 marks.*—The subject is treated under the headings: electrical units; conduction in electrolytes; experimental data of Kohlrausch and others; conductivity in other solvents, and the conductivity of liquid and solid electrolytes; diffusion of electrolytes and non-electrolytes; distribution equilibrium for electrolytes and non-electrolytes; electrode potentials and voltaic cells; gas cells, oxidation and reduction cells, storage batteries, etc.; electromotive behavior of alloys and amalgams; polarization; electrocapillary phenomena.

A fair knowledge of the subject, Faraday's law for instance, is presupposed in some parts of the book but not in others. The chapters on oxidation cells and on the electrocapillary phenomena are very good and the matter of alloys is treated at greater length than is usual. A special feature is the part on hydrated ions, p. 33, and on the relation between conductivity and fluidity, p. 41. The author adopts Liebenow's hypothesis of bivalent plumbite anions, PbO_2'', in his account of storage cells, p. 198; but this seems to the reviewer much less satisfactory than the hypothesis of quadrivalent lead. The difficulties in regard to 1.67 volts as the decomposition point for acids and bases are still unconquered. Owing to the author's objection to the osmotic pressure, he substitutes K the solubility constant of a metal for the solution pressure, P, of Nernst's formula, p. 130.

A book, which is avowedly mathematical, is never easy reading and no one should think of beginning a study of electrochemistry by reading van Laar's book. On the other hand, a number of things are presented in distinctly an interesting way, and the book is certainly worth while as supplementary reading. *Wilder D. Bancroft*

Übungsbeispiele aus der unorganischen Experimentalchemie. *By Heinrich Biltz and Wilhelm Biltz. 15 × 23 cm; pp. xi + 232. Leipzig: Wilhelm Engelmann, 1907. Price: bound, 7 marks.*—This is a manual of inorganic preparations and is not intended for beginners. The experiments are grouped as follows: elements; changes of state; simple compounds; compounds with a complex acid radical; compounds with a complex basic radical; complex non-electrolytes; preparation of compounds of the rare earths. The authors use the word ''complex'' as opposed to "simple," instead of as opposed to "double." The experiments are well chosen and the directions are complete so far as can be judged by reading them. The reviewer doubts the formation of manganate when ferromanganese is made anode in a cold caustic potash solution, but this is a trifling matter. The book will be valuable to the physical chemist and to the inorganic chemist alike and is a welcome addition to the literature. *Wilder D. Bancroft*

OSMOTIC PRESSURE

BY J. E. TREVOR

CONTENTS

Notation. Porter's equation for the osmotic pressure. The condition of osmotic equilibrium and Porter's equation. The dissipation of dilution. Relations of the osmotic pressure to the reversible and irreversible work and heat. The expression J for the dissipation. Derivatives of the osmotic pressure. Assuming incompressibility; relation to van't Hoff's theory. Other formulations of the temperature derivative. A correction. Summary.

Notation

p, pressure.
θ, absolute temperature.
M_1, Mass of solute in the solution.
M_2, mass of solvent in the solution.
m_1, composition of the solution—the ratio $M_1/(M_1 + M_2)$.

$\mu_2(p,\theta,m_1)$,	potential of the solvent in the solution.
$h_2(p,\theta)$,	specific thermodynamic potential of the solvent.
$h_a(p,\theta)$,	specific thermodynamic potential of the vapor of the solvent.
$v_2(p,\theta)$,	specific volume of the solvent.
$v_a(p,\theta)$,	specific volume of the vapor of the solvent.
$V(p,\theta,M_1,M_2)$,	volume of the solution.
$S(p,\theta,M_1,M_2)$,	entropy of the solution.
Δ,	an operator, forming the change, of the quantity operated on, when the solution of M_1 in M_2 is formed at p,θ from its components. Thus, writing v_1 for the specific volume of the solute, $\Delta V = V - M_1 v_1 - M_2 v_2$. The symbols ΔV, ΔS, ΔE, ΔF, ΔG, ΔH denote the corresponding changes of volume, entropy, energy, free energy, heat function, and thermodynamic potential. These quantities are functions of p,θ,M_1,M_2.
$\varphi_2(p,\theta,m_1)$,	the derivative $\partial V/\partial M_2$, which is identically $\partial \mu_2/\partial p$.
$\Delta_2(p,\theta,m_1)$,	the heat of dilution, $\partial \Delta G/\partial M_2$.
$p_o(\theta)$,	vapor pressure of the solvent.

$p_1(\theta,m_1)$,	vapor pressure of the solution.
$\mathrm{P}(p,\theta,m_1)$,	osmotic pressure of the solution.
r_2,	specific gas-constant of the solvent.
r,	molecular gas-constant.
w_1,	molecular weight of the solute.
w_2,	molecular weight of the solvent.
n,	$=\mathrm{M}_1/w_1$, the number of mols of solute in the solution.
N,	$=\mathrm{M}_2/w_2$, the number of mols of solvent in the solution.

Porter's equation for the osmotic pressure

This paper is concerned with the osmotic pressure P exerted, on an absolutely semipermeable wall, by a solution of an involatile solute. The relation between this pressure and the variables p,θ,m_1 on which it depends is the condition of osmotic equilibrium, that the potential of the solvent shall have the same value on each side of the osmotic wall,

$$\mu_2 = h_2(p-\mathrm{P},\theta).$$

This relation has been obtained by Prof. Alfred W. Porter[1] in an interesting form,

$$\int_{p_0}^{p-\mathrm{P}} v_2 dp = \int_{p_1}^{p} \phi_2 dp - \int_{p_1}^{p_0} v_a dp,$$

in which it is expressed by means of functions whose values are more or less readily determinable by experiment. Porter's equation was found by means of a rather complicated isothermal reversible cycle, in which solvent is obtained from the solution through an osmotic wall, and is then expanded, vaporized, expanded to the vapor pressure of the solution, and condensed upon the expanded solution; recompression of the solution restoring the initial state of the system.

This deduction is sound, but cumbrous. It involves the formulation of many successive steps; it fails to establish the connection of the result with the most fundamental form of the relation, namely the condition of osmotic equilibrium; and it does not exhibit the relation between the osmotic pressure and what I have called the 'dissipation of dilution,'

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[1] Proc. Roy. Soc. 79, 519 (1097).

the dissipatible part of the work development of a reversible dilution,—whereby it fails to bring the osmotic pressure into connection with the reversible and irreversible work and heat of a dilution of the solution. Such defects are characteristic of the reversible cycle method. For these reasons it is of interest to show that Porter's form of the osmotic pressure equation is an immediate consequence of the condition of osmotic equilibrium, taken in conjunction with the conditions of equilibrium for coexistent solution and vapor and for coexistent solvent and vapor, and that the dissipation of dilution is represented by the expression

$$\int_{p-\mathrm{P}}^{p} v_2 dp.$$

The condition of osmotic equilibrium and Porter's equation

Consider the solution, under the pressure p, to be in osmotic equilibrium with pure solvent. The pressure on the solvent will be p—P. In this case the condition of osmotic equilibrium is

$$h_2(p-\mathrm{P},\theta)-\mu_2(p,\theta,m_1)=0,$$

the condition of equilibrium for coexistent solution and vapor is

$$\mu_2(p_1,\theta,m_1)-h_a(p_1,\theta)=0,$$

and the condition (the special case for $m_1=0$) for coexistent solvent and vapor is

$$h_a(p_0,\theta)-h_2(p_0,\theta)=0.$$

Adding these equations,

$$\int_{p_0}^{p-\mathrm{P}}\frac{\partial h_2}{\partial p}dp=\int_{p_1}^{p}\frac{\partial \mu_2}{\partial p}dp-\int_{p_1}^{p_0}\frac{\partial h_a}{\partial p}dp\,;$$

or, noting that $\partial\mu_2/\partial p=\partial \mathrm{V}/\partial \mathrm{M}_2=\phi_2$,

$$(1)\qquad \int_{p_0}^{p-\mathrm{P}} v_2 dp=\int_{p_1}^{p}\phi_2 dp-\int_{p_1}^{p_0} v_a dp,$$

which is Porter's equation.

It will be noted that this equation yields explicit formulation of P only if it is found that the equation

$$\int v_2 dp = u_1(p,\theta)$$

can be solved for

$$p = u_2(u_1,\theta).$$

The dissipation of dilution

In the irreversible dilution of the solution, the rate of dissipation of energy per unit increase at p,θ of the mass of solvent in the solution is

$$-(\mu_2 - h_2).$$

This quantity[1] is the part of the reversible work development that is developed as heat when unit mass of the solvent is irreversibly added to a relatively great mass of the solution at p,θ. The relation of the osmotic pressure to this 'dissipation of dilution' is easily deducible from the condition of osmotic equilibrium alone,

$$\mu_2 = h_2(p - \mathrm{P},\theta)$$
$$= h_2 + \int_p^{p-\mathrm{P}} v_2 dp.$$

For, by simple rearrangement, we find

$$(2) \qquad -(\mu_2 - h_2) = \int_{p-\mathrm{P}}^{p} v_2 dp.$$

Relations of the osmotic pressure to the reversible and irreversible work and heat

Since equation (2) connects the osmotic pressure with the dissipation, we are enabled to connect this pressure with the rates of addition of reversible and irreversible work and heat, per unit increase at p,θ of the mass of solvent in the solution. When, in the relations[2] between these quantities and the dissipation, we replace the dissipation by the second member of (2), we obtain:

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[1] See this Journal, 10, 395–396 (1906).

[2] Ibid., 10, 400 (1906).

$$\text{Dissipation,}\quad -\frac{\partial \Delta H}{\partial M_2} = \int_{p-P}^{p} v_2 dp$$

$$\text{Irr. work,}\quad -p\frac{\partial \Delta V}{\partial M_2} = p\frac{\partial}{\partial p}\int_{p-P}^{p} v_2 dp$$

$$\text{Rev. heat,}\quad \theta\frac{\partial \Delta S}{\partial M_2} = \theta\frac{\partial}{\partial \theta}\int_{p-P}^{p} v_2 dp$$

$$\text{Rev. work,}\quad \frac{\partial \Delta F}{\partial M_2} = p^2\frac{\partial}{\partial p}\frac{1}{p}\int_{p-P}^{p} v_2 dp$$

$$\text{Irr. heat,}\quad \frac{\partial \Delta G}{\partial M_2} = \theta^2\frac{\partial}{\partial \theta}\frac{1}{\theta}\int_{p-P}^{p} v_2 dp.$$

The last of these equations is especially interesting, in that it connects the osmotic pressure with the heat of dilution, $\partial \Delta G/\partial M_2 = \Delta_2(p,\theta,m_1)$, which is the heat absorbed in the irreversible addition of unit mass of solvent to a relatively great mass of the solution at p,θ.

The last two of the above equations present aspects of the related circumstances that, speaking of *development* of work and heat,

Rev. work = *Irr. work* + *Dissipation*
Irr. heat = *Rev. heat* + *Dissipation.*

Other aspects are presented by the remaining relations[1] between these quantities:

$$\frac{\partial \Delta E}{\partial M_2} = -p\frac{\partial \Delta V}{\partial M_2} - \int_{p-P}^{p} v_2 dp + \theta\frac{\partial \Delta S}{\partial M_2}$$

$$\frac{\partial \Delta E}{\partial M_2} = +\frac{\partial \Delta F}{\partial M_2} + \int_{p-P}^{p} v_2 dp + \Delta_2$$

$$0 = +\frac{\partial \Delta F}{\partial M_2} + \int_{p-P}^{p} v_2 dp + p\frac{\partial \Delta V}{\partial M_2}$$

$$0 = -\int_{p-P}^{p} v_2 dp + \theta\frac{\partial \Delta S}{\partial M_2} - \Delta_2.$$

The expression J for the dissipation

Since Porter's equation

$$\int_{p_0}^{p-P} v_2 dp = \int_{p_1}^{p} \phi_2 dp - \int_{p_1}^{p_0} v_a dp,$$

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[1] See This Journal, 10, 396 (1906).

may be written

$$\int_{p_0}^{p} v_2 dp + \int_{p}^{p-P} v_2 dp = \int_{p_1}^{p_0} \phi_2 dp + \int_{p_0}^{p} \phi_2 dp - \int_{p_1}^{p_0} v_a dp,$$

we have

$$\int_{p-P}^{p} v_2 dp = \int_{p_1}^{p_0} (v_a - \phi_2) dp + \int_{p_0}^{p} (v_2 - \phi_2) dp$$

$$= \mathrm{J}. \tag{3}$$

This form of Porter's equation might have been obtained by replacing the first member of (2) by the known expression[1] J for the dissipation. It is a suitable equation from which to deduce expressions for the derivatives of the function $\mathrm{P}(p, \theta, m_1)$. These expressions might be derived from Porter's form of the equation, or indeed through partial differentiation of the condition of osmotic equilibrium. But the work is simplified by making use of (3).

Let us begin by finding expressions for the first derivatives of J. From the equation[2]

$$d\Delta \mathrm{H} = \Delta \mathrm{V}.dp - \Delta \mathrm{S}.d\theta + (\mu_1 - h_1) d\mathrm{M}_1 - \mathrm{J} d\mathrm{M}_2,$$

we deduce

$$\frac{\partial \mathrm{J}}{\partial p} = -\frac{\partial \Delta \mathrm{V}}{\partial \mathrm{M}_2}$$

$$= -\phi_2 + v_2. \tag{4a}$$

We also deduce

$$\frac{\partial \mathrm{J}}{\partial \theta} = \frac{\partial \Delta \mathrm{S}}{\partial \mathrm{M}_2},$$

which transforms the relation between the irreversible and reversible heats of dilution and the dissipation,

$$\Delta_2 = \theta \frac{\partial \Delta \mathrm{S}}{\partial \mathrm{M}_2} - \mathrm{J},$$

to

$$\frac{\partial \mathrm{J}}{\partial \theta} = \frac{\Delta_2}{\theta} + \frac{\mathrm{J}}{\theta}. \tag{4b}$$

These familiar equations must now be supplemented by an equation for $\partial \mathrm{J}/\partial m_1$. Differentiating J with regard to m_1, and noting that $\phi_2 = \partial \mu_2 / \partial p$,

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[1] As in this Journal, 10, 399 (1906).

[2] This Journal, 10, 399 (1906).

$$\frac{\partial J}{\partial m_1} = \frac{\partial}{\partial m_1}\left(h_a(p_0,\theta) - h_a(p_1,\theta) + \int_{p_0}^{p} v_2 dp - \int_{p_1}^{p} \phi_2 dp\right)$$

$$= - v_a(p_1,\theta)\,\frac{\partial p_1}{\partial m_1} - \frac{\partial}{\partial m_1}\int_{p_1}^{p}\frac{\partial \mu_2}{\partial p}\,dp$$

$$= - v_a(p_1,\theta)\,\frac{\partial p_1}{\partial m_1} - \frac{\partial \mu_2}{\partial m_1} + \frac{\partial \mu_2(p_1,\theta,m_1)}{\partial p_1}\,\frac{\partial p_1}{\partial m_1} + \frac{\partial \mu_2(p_1,\theta,m_1)}{\partial m_1}$$

$$(4c) = - \left(v_a(p_1,\theta) - \phi_2(p_1,\theta,m_1)\right)\frac{\partial p_1}{\partial m_1} - \int_{p_1}^{p}\frac{\partial \phi_2}{\partial m_1}\,dp.$$

Derivatives of the osmotic pressure

We are now to seek expressions for the first derivatives of $P(p,\theta,m_1)$, through partial differentiation of

$$(a) \qquad J = \int_{p-P}^{p} v_2 dp.$$

Differentiating with regard to p, and substituting (4*a*),

$$\frac{\partial J}{\partial p} = \frac{\partial}{\partial p}\left(h_2 - h_2(p - P,\theta)\right)$$

$$-\phi_2 + v_2 = v_2 - v_2(p - P,\theta)\left(1 - \frac{\partial P}{\partial p}\right);$$

whence

$$(5a) \qquad v_2(p - P,\theta)\,\frac{\partial P}{\partial p} = v_2(p - P,\theta) - \phi_2.$$

This is Porter's equation (6). It will be observed that under any ordinary conditions the value of $\partial P/\partial p$ is very small.

Differentiating (*a*) with regard to θ, and substituting (4*b*),

$$\frac{\partial J}{\partial \theta} = \frac{\partial}{\partial \theta}\left(h_2 - h_2(p - P,\theta)\right)$$

$$\frac{\Delta_2}{\theta} + \frac{J}{\theta} = \frac{\partial h_2}{\partial \theta} + v_2(p - P,\theta)\frac{\partial P}{\partial \theta} - \frac{\partial h_2(p - P,\theta)}{\partial \theta}$$

$$\frac{\Delta_2}{\theta} + \frac{1}{\theta}\int_{p-P}^{p} v_2 dp = \int_{p-P}^{p}\frac{\partial^2 h_2}{\partial p\,\partial \theta}\,dp + v_2(p - P,\theta)\,\frac{\partial P}{\partial \theta}$$

$$= \int_{p-P}^{p}\frac{\partial v_2}{\partial \theta}\,dp + v_2(p - P,\theta)\,\frac{\partial P}{\partial \theta}.$$

Solving for $\partial P/\partial\theta$,

$$v_2(p-P,\theta)\,\frac{\partial P}{\partial\theta}=\frac{\Delta_2}{\theta}-\theta\int_{p-P}^{p}\frac{\partial}{\partial\theta}\,\frac{v_2}{\theta}\,dp. \tag{5b}$$

Differentiating (a) with regard to m_1, and substituting (4c),

$$\frac{\partial J}{\partial m_1}=\frac{\partial}{\partial m_1}\Big(h_2-h_2(p-P,\theta)\Big)$$

$$-\Big(v_a(p_1,\theta)-\phi_2(p_1,\theta,m_1)\Big)\frac{\partial p_1}{\partial m_1}-\int_{p_1}^{p}\frac{\partial\phi_2}{\partial m_1}\,dp=v_2(p-P,\theta)\,\frac{\partial P}{\partial m_1}. \tag{5c}$$

From this formulation it appears that the rate of change of the osmotic pressure with the composition at constant imposed pressure and temperature is a definite positive quantity, less a small correcting term; and that the major term depends largely on the relation of the vapor pressure of the solution to the composition.

Assembling the expressions just found, we have:

$$v_2(p-P,\theta)\,\frac{\partial P}{\partial p}=v_2(p-P,\theta)-\phi_2$$

$$v_2(p-P,\theta)\,\frac{\partial P}{\partial\theta}=\frac{\Delta_2}{\theta}-\theta\int_{p-P}^{p}\frac{\partial}{\partial\theta}\,\frac{v_2}{\theta}\,dp$$

$$v_2(p-P,\theta)\,\frac{\partial P}{\partial m_1}=-\Big(v_a(p_1,\theta)-\phi_2(p_1,\theta,m_1)\Big)\frac{\partial p_1}{\partial m_1}-\int_{p_1}^{p}\frac{\partial\phi_2}{\partial m_1}\,dp.$$

Assuming Incompressibility. Relation to van't Hoff's theory

All the relations of the theory of the osmotic pressure, as detailed in the foregoing, are much simplified by the single assumption that the solvent is incompressible, that $\partial v_2/\partial p=0$. For then the dissipation

$$\int_{p-P}^{p}v_2dp$$

becomes Pv_2, and this quantity can be substituted for the above integral in all the equations of the theory.

It is obvious to remark that, when both solvent and solution are assumed to be incompressible, Porter's equation, in the form (3),

$$\int_{p-\mathrm{P}}^{p} v_2 dp = \int_{p_1}^{p_0} (v_a - \phi_2) dp + \int_{p_0}^{p} (v_2 - \phi_2) dp,$$

supplies for the osmotic pressure the simple expression[1]

$$\mathrm{P}v_2 = \int_{p_1}^{p_0} v_a dp + (p - p_0)v_2 - (p - p_1)\phi_2.$$

The integral here can be evaluated by means of a good interpolation formula for v_a; and ϕ_2 can be obtained from the density d of the solution and the change of the density with the composition,

$$\phi_2 = \frac{1}{d} + \frac{m_1}{d^2}\frac{\partial d}{\partial m_1}.$$

Or, what is the same thing, by utilizing the observed rate of change of the specific volume v of the solution with the composition, ϕ_2 may be found by means of the relation

$$\phi_2 = v - \frac{\partial v}{\partial m_1} m_1.$$

Under the corresponding extensive assumptions, van't Hoff's law connecting the vapor pressure of the solution with the composition may be obtained from the osmotic pressure equation. Assuming the solvent to be incompressible, neglecting the small quantity

$$(p - p_0)v_2 - \int_{p_1}^{p} \phi_2 dp,$$

and taking $v_a = r_2\theta/p$, the equation, in the form (3), becomes

$$\mathrm{P}v_2 = r_2\theta \log(p_0/p_1).$$

The mass M_1 being n mols of the solute, the volume of the mass of solvent in which one mol of solute is dissolved in the solution is $v_2\mathrm{M}_2/n$. Making van't Hoff's further assumption that

$$\mathrm{P}\frac{v_2\mathrm{M}_2}{n} = r\theta,$$

or

$$\mathrm{P}v_2 = (n/\mathrm{N})r_2\theta,$$

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[1] If V does not contain p, neither does $\phi_2 = \partial \mathrm{V}/\partial \mathrm{M}_2$.

elimination of $Pv_2/r_2\theta$ yields van't Hoff's law,

$$\log\frac{p_0}{p_1}=\frac{n}{N}.$$

It may here be noted that, if we assume zero heat of dilution by an incompressible solvent, the equation (5*b*) for the temperature derivative of the osmotic pressure yields

$$\frac{\partial Pv_2}{\partial\theta}=\frac{Pv_2}{\theta},$$

which asserts the quantity Pv_2 to be proportional to θ. And we may note further that, when *constant* v_2 and zero heat of dilution are assumed, the equation becomes

$$\frac{\partial P}{\partial\theta}=\frac{P}{\theta},$$

asserting that P is proportional to θ.

Let us now examine the connection between the general equation (5*c*), for the composition derivative of P, and the van't Hoff theory of the osmotic pressure. We may do this by calculating the value given by the van't Hoff theory for the quantity

$$\frac{\partial P/\partial m_1}{\partial\log p_1/\partial m_1}.$$

In this theory we have, as already noted,

$$\frac{P.v_2M_2}{n}=r\theta;$$

whence

$$P=\frac{r}{w_1}\frac{M_1}{M_2}\frac{\theta}{v_2}$$

$$=\frac{r}{w_1}\frac{m_1}{1-m_1}\frac{\theta}{v_2}$$

$$(c)\qquad \frac{\partial P}{\partial m_1}=\frac{w_2}{w_1}\frac{r_2}{v_2}\frac{\theta}{(1-m_1)^2}.$$

To find $\partial\log p_1/\partial m_1$ in the van't Hoff theory, we have, as already noted,

$$\log\frac{p_0}{p_1}=\frac{n}{N}=\frac{w_2}{w_1}\frac{M_1}{M_2}=\frac{w_2}{w_1}\frac{m_1}{1-m_1}$$

$$(d)\qquad \frac{\partial\log p_1}{\partial m_1}=-\frac{w_2}{w_1}\frac{1}{(1-m_1)^2}$$

Combining (*c*) and (*d*),

$$\frac{\partial P/\partial m_1}{\partial \log p_1/\partial m_1} = -\frac{r_2\theta}{v_2}.$$

This equation of van't Hoff's theory follows from the general equation (5*c*) when we neglect the small 'correcting term,' assume v_2 to be independent of p, neglect ϕ_2 in comparison with v_a, and assume $p_1 . v_a(p_1,\theta) = r_2\theta$. Neglect of the correcting term is equivalent to assuming $\partial\phi_2/\partial m_1 = 0$, which is equivalent to assuming $\partial^2 v/\partial m_1{}^2 = 0$, which is equivalent to the assumption that the specific volume $v(p,\theta,m_1)$ of the solution is linear in the composition.

Other formulations of the temperature derivative

In the equation (5*b*) for the temperature derivative of the osmotic pressure,

$$v_2(p - P,\theta)\frac{\partial P}{\partial\theta} + \theta\int_{p-P}^{p}\frac{\partial}{\partial\theta}\frac{v_2}{\theta}\,dp = \frac{\Delta_2}{\theta},$$

the heat of dilution $\Delta_2(p,\theta,m_1)$ may be expressed by means of the functions v_a, v_2, ϕ_2, p_0, p_1, whose values are more or less readily determinable by experiment. If we expand the general equation for Δ_2,

$$\frac{\Delta_2}{\theta} = \theta\frac{\partial}{\partial\theta}\frac{J}{\theta},$$

and write A for the quantity

$$\Big(v_a(p_0,\theta) - v_2(p_0,\theta)\Big)\frac{dp_0}{d\theta} - \Big(v_a(p_1,\theta) - \phi_2(p_1,\theta,m_1)\Big)\frac{\partial p_1}{\partial\theta},$$

we find

$$(e) \qquad \frac{\Delta_2}{\theta} = A + \theta\int_{p_1}^{p_0}\frac{\partial}{\partial\theta}\frac{v_a - \phi_2}{\theta}\,dp + \int_{p_0}^{p}\frac{\partial}{\partial\theta}\frac{v_2 - \phi_2}{\theta}\,dp.$$

It may be remarked that if we take $p = p_1$, neglect v_2, ϕ_2 in comparison with v_a, and assume $pv_a = r_2\theta$, this equation reduces to Kirchhoff's equation for the heat of dilution,

$$\frac{\Delta_2}{\theta} = r_2\theta\frac{\partial}{\partial\theta}\log\frac{p_0}{p_1}.$$

When Δ_2 is expressed as in (*e*), the equation (5*b*) becomes

$$v_2(p-\mathrm{P},\theta)\frac{\partial \mathrm{P}}{\partial\theta}+\theta\int_{p-\mathrm{P}}^{p}\frac{\partial}{\partial\theta}\frac{v_2}{\theta}\,dp=\mathrm{A}+\theta\int_{p_1}^{p_0}\frac{\partial}{\partial\theta}\frac{v_a-\phi_2}{\theta}\,dp$$
$$+\theta\int_{p_0}^{p}\frac{\partial}{\partial\theta}\frac{v_2-\phi_2}{\theta}\,dp.$$

The form of this equation may be somewhat simplified by adding to it the equation for the dissipation of dilution,

$$\int_{p-\mathrm{P}}^{p}v_2dp=\mathrm{J}.$$

For it then becomes

$$v_2(p-\mathrm{P},\theta)\frac{\partial \mathrm{P}}{\partial\theta}+\int_{p-\mathrm{P}}^{p}\frac{\partial v_2}{\partial\theta}dp=\mathrm{A}+\int_{p_1}^{p_0}\frac{\partial(v_a-\phi_2)}{\partial\theta}\,dp+\int_{p_0}^{p}\frac{\partial(v_2-\phi_2)}{\partial\theta}\,dp.$$

This is the form that immediately results when the three conditions of equilibrium

$$\mu_2-h_2(p-\mathrm{P},\theta)=0$$
$$h_a(p_1,\theta)-\mu_2(p_1,\theta,m_1)=0$$
$$h_2(p_0,\theta)-h_a(p_0,\theta)=0$$

are added, and the resulting equation is differentiated with regard to θ.

A correction

In my paper "On the General Equations of the Theory of Solutions,"[1] to which reference has been made in the foregoing, the equation (17) for the osmotic pressure was deduced under the tacit assumption that the pressure sustained by the solution is the same as that supported by the coexistent solvent beyond the osmotic wall. This error requires correction. If p be the pressure sustained by the solution, the pressure on the coexistent solvent is $p-\mathrm{P}$. Let, now, an infinitesimal decrease of the applied pressure P effect addition of the mass $d\mathrm{M}_2$ of solvent to the solution at constant p,θ,M_1.

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[1] This Journal, 10, 392 (1906).

Before this addition, the energy of the system composed of the masses

$$M_1 + M_2 \text{ and } dM_2$$

is

$$E + e_2(p - P,\theta)dM_2.$$

After the addition, the energy of the system is

$$E + \left\{ e_2(p-P,\theta) - P\frac{\partial V}{\partial M_2} - (p-P)\left(\frac{\partial V}{\partial M_2} - v_2(p-P,\theta)\right) \right.$$
$$\left. + \theta\left(\frac{\partial S}{\partial M_2} - s_2(p-P,\theta)\right)\right\} dM_2,$$

employing the notation of the previous paper. The initial energy of the solution was E. So the rate of increase of the energy of the solution is

$$\frac{\partial E}{\partial M_2} = e_2(p - P,\theta) - P\frac{\partial V}{\partial M_2} - (p - P)\left(\frac{\partial V}{\partial M_2} - v_2(p - P,\theta)\right)$$
$$+ \theta\left(\frac{\partial S}{\partial M_2} - s_2(p - P,\theta)\right).$$

Here

$$\frac{\partial E}{\partial M_2} = -p\frac{\partial V}{\partial M_2} + \theta\frac{\partial S}{\partial M_2} + \mu_2;$$

wherefore, by subtraction,

$$\mu_2 = e_2(p - P,\theta) + (p - P).v_2(p - P,\theta) - \theta.s_2(p - P,\theta).$$

This is the condition of osmotic equilibrium,

$$\mu_2 = h_2(p - P,\theta),$$

that the potential of the solvent shall have the same value on each side of the osmotic wall. The former equation (17) obtained in place of this is incorrect.

Summary

The chief results of the present investigation may be summarized as follows:

For the osmotic pressure exerted, on an absolutely semipermeable wall, by a solution of an involatile solute, the equation deduced by Porter by means of a complicated cyclical operation is shown to be an immediate consequence of the condition of osmotic equilibrium, taken in conjunction with the conditions of equilibrium for coexistent solution and vapor and for coexistent solvent and vapor.

It is shown that the osmotic pressure is connected with the 'dissipation of dilution' ($-\partial\Delta H/\partial M_2$) by the equation

$$-\frac{\partial\Delta H}{\partial M_2}=\int_{p-P}^{p}v_2dp;$$

and the consequent relations of the osmotic pressure to the reversible and irreversible work and heat of a dilution are formulated.

Relatively simple expressions are obtained for the rate of change of the osmotic pressure with the temperature at constant pressure and composition of the solution, and with the composition at constant pressure and temperature of the solution; the implications of van't Hoff's theory of dilute solutions are compared with these results; and it is shown that zero heat of dilution and constant specific volume of the solvent are conditions sufficient to ensure proportionality of the osmotic pressure with the absolute temperature.

Recognition of an oversight in a previous calculation leads to a deduction of the condition of osmotic equilibrium.

Cornell University,
Jan. 18, 1908.

A HYDROGEN PEROXIDE CELL

BY H. T. BARNES AND G. W. SHEARER

The behaviour of aluminum and magnesium electrodes in water containing dissolved air, oxygen or hydrogen peroxide was first studied by one of the authors in conjunction with H. M. Tory[1] and G. H. Cole.[2] It was shown that an abnormally high electromotive force was developed between these two metals, which was connected with the presence of free oxygen in the water. Without oxygen only a small electromotive force existed, but the dissolving of so small an amount of that gas as could be obtained by bubbling air through the initially depleted water caused the voltage to rise from 0.02 to about one volt. The effect was traced to the aluminum electrode alone by measuring the electromotive force between two electrodes of the same metal in a cell divided into two compartments, one containing water free from air, and the other containing air-charged water. In every case the metal in the dissolved oxygen was the cathode. A number of metals was studied in this way, and a large or small effect observed. Aluminum, however, was conspicuous by the magnitude of the effect, and an electromotive force of nearly a volt could be maintained between two electrodes of aluminum, due merely to the action of the dissolved air.

Fig. 1 shows the two types of cells used to study this effect. In A the vessel was a long glass tube with inlet holes at top and bottom, and an outlet hole in the middle. Air-free water from a flask of boiling water was let in at the top at any desired temperature, and air-charged water was let in at the bottom. Both streams flowed out the central orifice, where a line of separation was sharply maintained. The tube could also be completely flushed out, either with air-free or air-charged water. The electrodes passed through corks at

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[1] Trans. Am. Electrochem. Soc., 3, 95 (1903).

[2] Ibid., 12, 54 (1907).

the top and bottom, and the difference of potential was measured on an electrometer. In the type B, two compartments were provided with inclined side tubes into which various electrodes could be thrust. Air-free or air-charged water was run continuously through the compartments. The latter form was found more convenient when working with water at the same temperature in both sides.

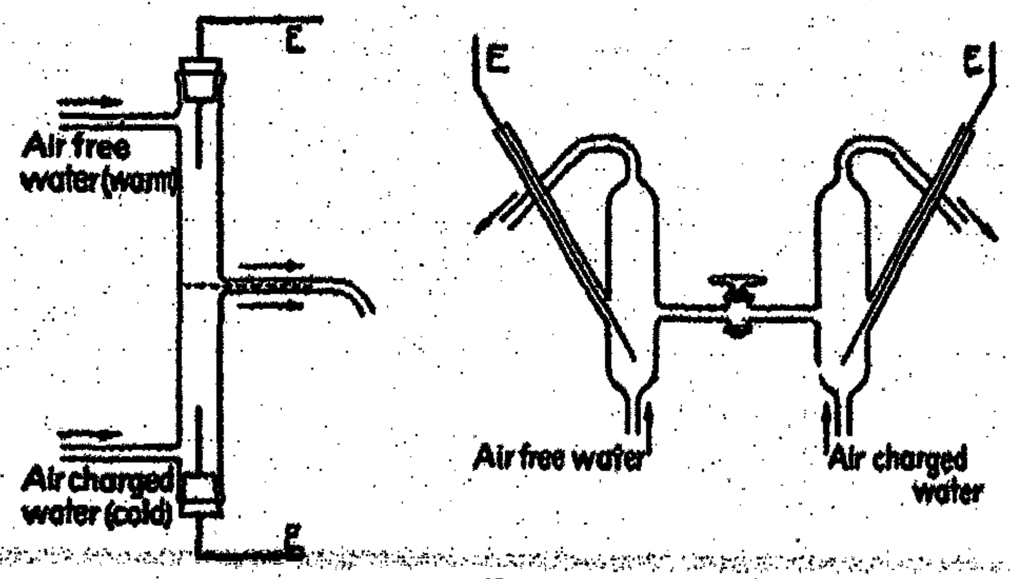

Fig. 1

It was found that the effect produced on different metals was additive, so that selecting a metal like magnesium high up in the electro-positive series which showed practically no difference in air-free or air-charged water, it was possible to get the effect of oxygen on any metal by measuring it against this metal in a single cell. Thus we selected the combination of magnesium with aluminum to further study the electromotive force produced in different electrolytes. As a cell it was found that the best results were obtained with a combination of

$$Mg — Al_2(SO_4)_3 — Al$$

and that a considerable current could be obtained from the cell. With the addition of hydrogen peroxide, the electromotive force was further augmented to 1.7 and even to 2.1 volts.

A peculiar feature of this cell was a rise of electromotive force and current on closed circuit for a considerable time, and after passing through a maximum value, a gradual fall in value, but adding fresh hydrogen peroxide always sent the electromotive force and current up again to the maximum values. It was evident from early experiments[1] that, on account of the direction of the current in the cell, the gradual rise was associated with the removal of the high resistance surface film from the aluminum, thereby exposing a clean surface of the metal, and that the fall was associated with a depletion of the H_2O_2, or oxygen ions, around the aluminum surface. Shaking the cell always sent the electromotive force up a little, but not so much as adding H_2O_2.

It is well known that aluminum as cathode allows current to pass freely, but as anode shows an abnormally high resistance. This has been fairly conclusively shown to be due to the formation of a thin film of hydroxide on the aluminum surface in the latter case, and its removal in the former.

Our cell behaved to outside currents just as we would expect if this were true. A current from a powerful storage battery sent for a short time through the cell so as to make the aluminum the cathode, left the electromotive force of the cell at its high maximum value, while when passed in the other direction so as to form the anode film on the aluminum, left the electromotive force at its low initial value.

The question of the gradual rise of electromotive force and current in the cell was, therefore, not difficult to explain, but the abnormally high electromotive force produced between the two metals otherwise close together in the electrochemical series was not so easy to explain until Professor Bancroft suggested to one of the authors, that possibly the aluminum in the presence of dissolved oxygen generated H_2O_2, and thereby formed a cell with H_2O_2 as electrode. The reaction, he suggested, might take place as follows:

$$2Al + 6H_2O + 6O = Al_2(OH)_6 + 3H_2O_2.$$

In this case, as soon as an aluminum plate was placed in water containing dissolved oxygen, the surface was oxidized and H_2O_2 generated. In order to test this point we placed

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[1] Loc. cit., page 58.

some pure aluminum sheet in ordinary pure distilled water open to the air and thoroughly charged and after standing a few hours we applied the well-known KI and starch test for the peroxide with marked success. There was a comparatively strong reaction for hydrogen peroxide, while some of the same sample of water not in contact with aluminum showed absolutely no trace.

Having obtained evidence of the production of the peroxide, we found that the yield could be increased by using a considerable quantity of aluminum foil in small pieces and leaving it for two or three days in water through which air was bubbled. Mechanical agitation also helped the production. We obtained the greatest yield when we cooled the water by immersing the flask in cracked ice and at the same time sent a current through the water, making the mass of aluminum foil the anode and having a small aluminum wire as cathode. In this way we obtained a starch reaction of about the same apparent strength as a solution of the ordinary 3 percent hydrogen peroxide made up to a dilution of 1 or 2 drops in a liter of water. If a current was sent through the water so as to make the aluminum the cathode, no reaction for the peroxide could be obtained. In this case an anode of platinum was used.

The dependence of the hydrogen peroxide upon the presence of dissolved oxygen was shown very completely by the following test: A quantity of pure aluminum foil was boiled in distilled water. The heat was then removed and the flask tightly corked and allowed to cool for several hours. On opening the flask the water was quickly poured off from the foil and tested for peroxide without success. The same foil, however, when placed in water containing air developed H_2O_2 at once.

Tests on the Peroxide Cell with Aluminum and Magnesium Electrodes

The fact that aluminum metal develops hydrogen peroxide in contact with water, and free oxygen is sufficient to explain the abnormally high electromotive force that exists between aluminum and magnesium as well as other combinations. In the cell containing these electrodes as studied by one of us with Mr. Cole, the addition of H_2O_2 serves merely to increase the concentration of the peroxide around the aluminum and thus to increase the effect. When the cell supplies current, the cathodic action of the aluminum is to remove the surface film and to decompose the peroxide. The first action is accompanied by an increase in electromotive force and current, and the depletion of peroxide is the cause of the slow falling off in electromotive force and current after the maximum value has been reached. The energy of the cell is at the expense of the magnesium which is changed to the hydroxide. We have represented in the following curves some of the tests on the cell, with and without hydrogen peroxide, and the effect of temperature.

Fig. 2 represents the rate of rise of current and voltage in a cell to which no H_2O_2 has been added. The first portion of the scale is in hours up to 2 from which point on the time is expressed in minutes. The addition of 40 cc of the ordinary 3 percent H_2O_2 is shown by the sudden rapid rise both in current and in electromotive force. A very rapid fall is

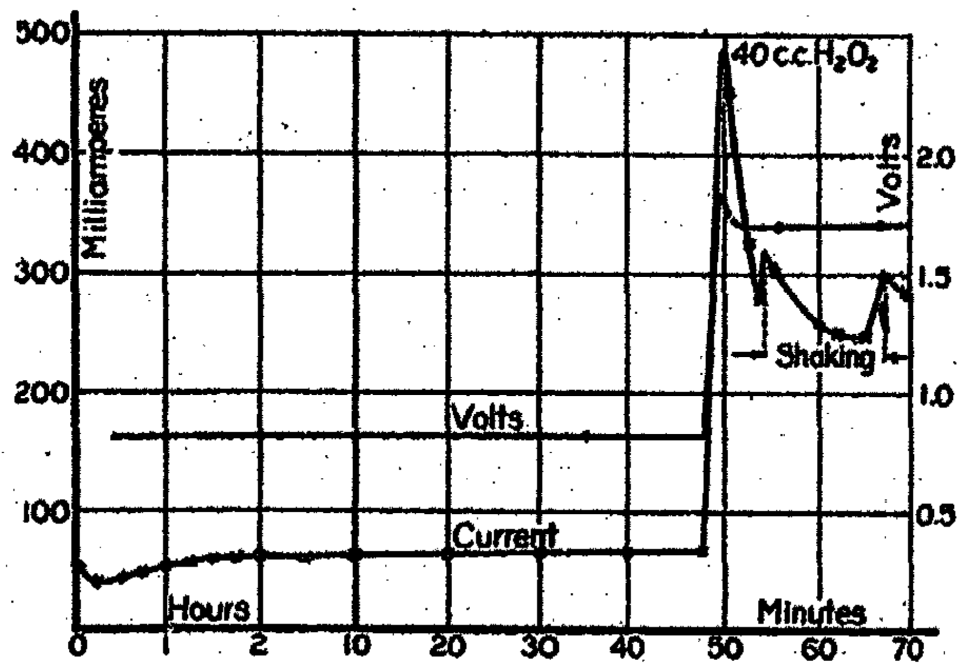

Fig. 2

shown to take place, after which a more gradual drop follows. The effect of shaking the cell is shown at two points. The voltmeter readings were not taken often enough for a complete curve. In the previous paper with Mr. Cole complete voltage and current curves are given for a special form of this cell.

Fig. 3 shows the effect of temperature on the voltage and current from the cell with no H_2O_2 added. At the point marked "heat removed," the cell was at the boiling-point and then allowed to cool. The current increased very rapidly with temperature from 0.14 ampere to nearly an ampere. At the boiling-point the effervescence became quite violent.

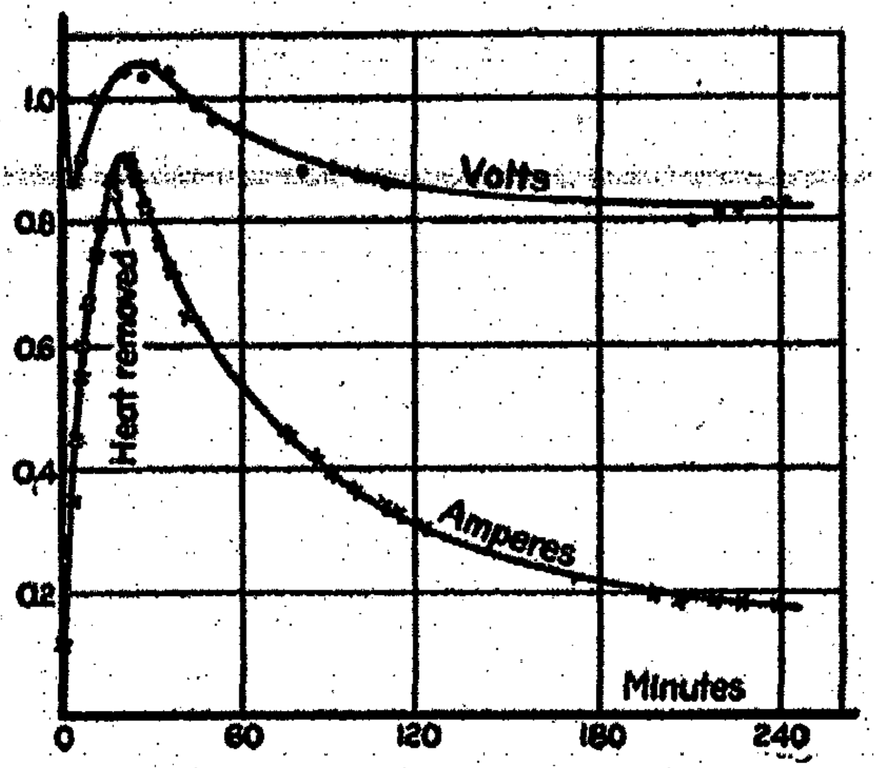

Fig. 3

Fig. 4 shows a similar set of readings, but in addition 20 cc of the 3 percent H_2O_2 was added when the cell was at the boiling-point. A sudden rise both in voltage and in current is then followed by as sudden a drop to normal conditions, probably owing to the rapid decomposition of the H_2O_2.

Fig. 5 shows the electromotive force and current curves on a temperature base with no H_2O_2 added.

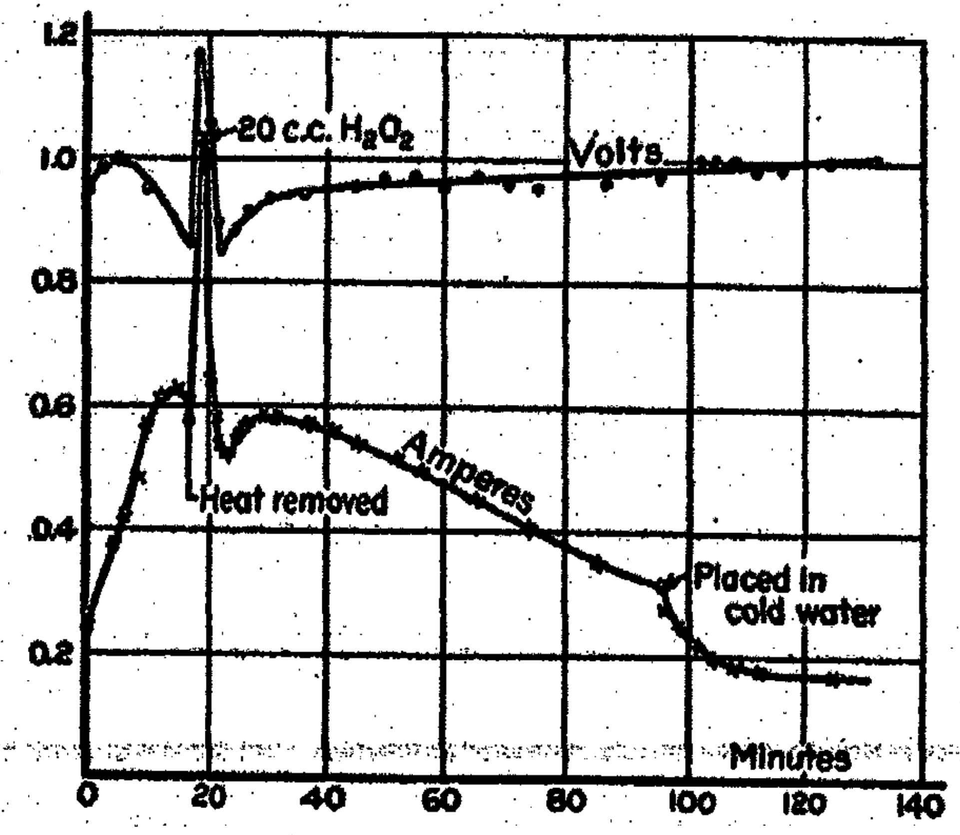

Fig. 4

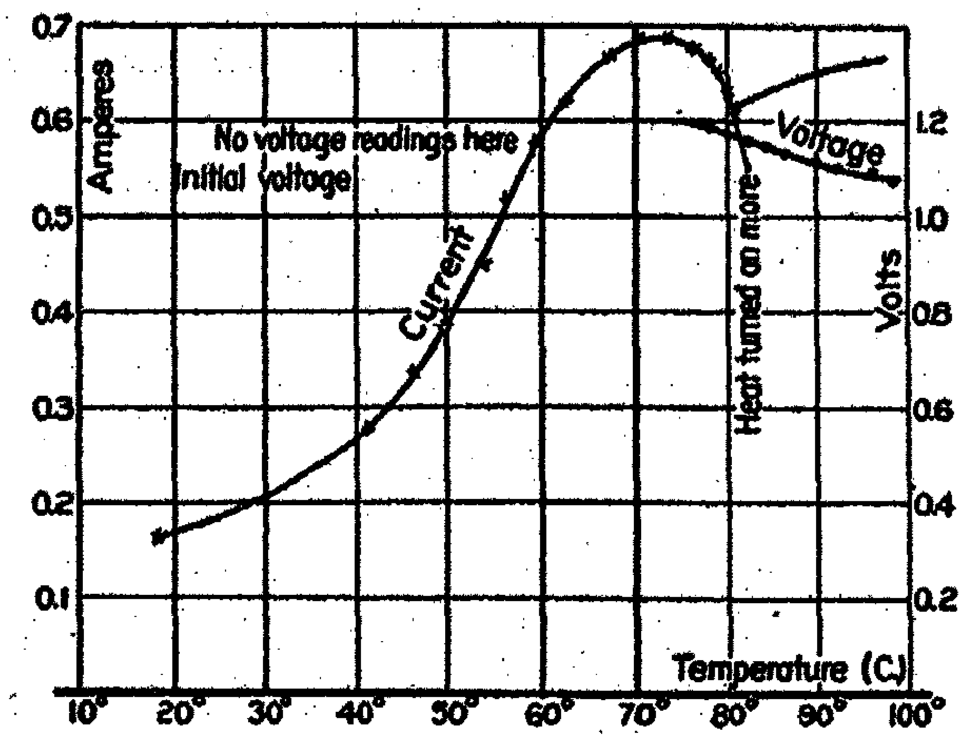

Fig. 5

Conclusion

We have concluded from this and previous studies of aluminum electrodes that a surface film is formed over all surfaces of this metal exposed to air or water and that the reaction in the case of water develops hydrogen peroxide.

The presence of the peroxide thus formed explains the peculiar behaviour of the aluminum and magnesium cell. The reaction between aluminum and water is such as to suggest a composition for the surface film of $Al_2(OH)_6$.

Although it has been stated that hydrogen peroxide is produced from several metals in contact with water, notably zinc and iron, we were unable to detect it in the case of zinc, treated in a similar way to our aluminum metal. If dissolved air produces a similar effect on other metals and thus gives rise to the potential effects which we observed on nearly all the metals examined, then it is likely to be too small in amount to be detected by the starch and iodine reaction.

McGill University,
Dec. 16, 1907.

THE HEATS OF VAPORIZATION OF THE LIQUID HALOGEN HYDRIDES AND OF SULPHURETTED HYDROGEN

BY P. H. ELLIOTT AND D. McINTOSH

Steele and McIntosh[1] have calculated the value of the heats of vaporization of the hydrides of the halogens, of sulphur and of phosphorus from the slope of the vapor pressure curve, by means of the well-known Clausius equation

$$\frac{dp}{dT} = \frac{PW}{RT^2}$$

where $\frac{dp}{dT}$ represents the change of pressure with temperature, P the vapor pressure, R the gas constant, T the temperature on the absolute scale, and W the latent heat of vaporization. Being unaware of any direct measurements of the values of W we have attempted to determine these in a simple way. This was undertaken, not merely to ascertain whether the calculated values were correct, but on account of another research for which a fairly accurate knowledge of these numbers was of importance.

Method and Apparatus

The apparatus used was a modification of that described originally by Marshall and Ramsay, and since used by many investigators.[2] It is shown in the accompanying figure, and consists of a small Dewar tube (A) used to contain the liquid under examination. This vacuum vessel is closed by a double bored rubber stopper through which pass the leads of the heating coil enclosed in glass, and an arm fitted with a three-way tap (B), the tubes of which are bent and terminate in two small cups, one of which (C) is indicated in the figure. The electrical energy used to heat the coil was measured by Weston

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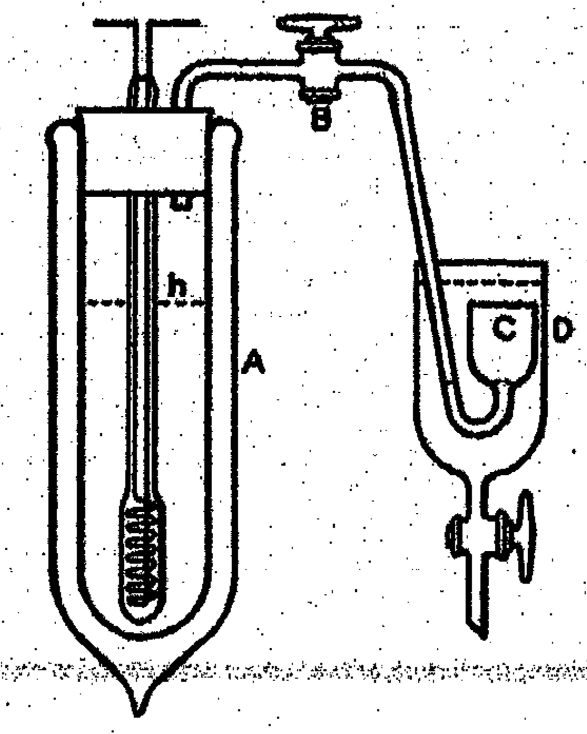
[1] Zeit. phys. Chem., 55, 139 (1906).

[2] See Franklin and Kraus: Jour. Phys. Chem., 11, 553 (1906).

instruments calibrated by means of a copper voltameter and a Weston cell.



Hydrogen Chloride

A few moistened beads[1] were placed in the bottom of the vacuum tube, and the apparatus was filled with the acid (boiling-point —83°) to about two inches above the heating coil. A little mercury was put in the cups, and these were immersed in funnel-shaped tubes (D) filled with water. The vacuum tube was placed in a bath of carbon dioxide and ether (boiling-point —78°) and a very small current[2] passed through the heating coil to prevent superheating. The acid boiled away and was absorbed by the water. When a steady rate of evaporation was reached, the tap was turned and the gas was absorbed for a five-minute period. (This vaporization we shall refer to as "natural evaporation.") The tap was again turned, a current of from 0.5 to 1 ampere passed through the coil for one minute, and the quantity of acid evaporated in five minutes was absorbed as before. In this way the "natural evaporation" was determined immediately before and after each experiment. Any great variation in this evaporation

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[1] Steele: Zeit. phys. Chem., 55, 171 (1906).

[2] The energy supplied was about two percent of that actually used in the experiment.

pointed to some source of error, and the determination was discarded. The acid was titrated with standard ammonia.

The results for hydrochloric acid were: 14.7, 14.8, 15.3; mean 14.9 × 10^{10} ergs for each gram molecule evaporated.

Hydrobromic Acid

The temperature of the carbonic acid bath being below the boiling-point of the hydrogen bromide, the vacuum vessel was covered with asbestos wound with fine platinum wire, through which a current sufficient to maintain slow evaporation was sent. In other respects the apparatus was the same as that previously described. The values found were 17.6, 17.3, 16.9; mean 17.3 × 10^{10} ergs per gram molecule

Hydriodic Acid

The calorimeter was placed inside a large silver vacuum vessel and covered with natural wool. The values given by these experiments were: 18.8, 18.9, 18.7; mean 18.8 × 10^{10} ergs for the vaporization of 128 grams of acid.

Hydrogen Sulphide

The apparatus employed was that used in the hydrobromic acid experiments. The gas was absorbed by a strong potassium hydrate solution in Geissler bulbs. The results were: 19.4, 19.4, 19.2, 20.3; mean 19.6 × 10^{10} ergs.

In all cases evaporation took place at pressures a little higher than that of the atmosphere, usually at 77 cm of mercury. The following table gives the values of W, calculated for 76 cm, and those found by experiment.

Calculated		Found
Hydrochloric Acid....	14.8 × 10^{10} ergs	14.9 × 10^{10} ergs
Hydrobromic "	17.4 × 10^{10} "	17.3 × 10^{10} "
Hydriodic "	20.7 × 10^{10} "	18.8 × 10^{10} "
Hydrogen sulphide....	19.3 × 10^{10} "	19.6 × 10^{10} "

The calculated values are in fair agreement with those determined experimentally except in the case of hydriodic acid. Whether this variation is due to an error in the determination of the vapour pressure curve, which seems unlikely, or to a defect in the method of measuring W, such as too large natural evaporation, we shall attempt to discover by new experiments.

The impossibility of determining W from the van't Hoff equation,

$$\frac{0.02\,T^2}{K} = W,$$

on account of the association or dissociation of the solutes has been pointed out in a previous paper.

McGill University, Montreal,
December, 1907.

THE HEAT OF FORMATION OF TETRAVALENT OXYGEN COMPOUNDS

BY D. MCINTOSH

When organic bodies containing oxygen are added to the liquefied halogen hydrides additive compounds are formed and a large amount of heat is evolved.[1] In a paper on the "Higher Valencies of Oxygen," Archibald and McIntosh[2] called attention to this, and in several instances, used the heat development to determine when the affinity of the acid was balanced by the oxygen compound. In the following pages I shall give a few measurements of the heat evolved during these reactions, and as heat evolution generally denotes chemical combination, the figures given may perhaps add something to the evidence in favour of the formation of tetravalent oxygen compounds.

Apparatus and Method

The apparatus used is shown in the figure and consists of a small Dewar test-tube, A, closed by a rubber stopper through which passes the tube B and an arm of the three-way tap C. The tube B has a glass point melted in at D, so that a small sealed bulb, E, containing the organic liquid used in the experiment may be held there, and is closed by a stopper carrying the stout glass rod F. G is a stirrer formed from a platinum wire to which is attached a glass tube, and a soft iron rod enclosed in glass; by aid of a small electro-magnet, this stirrer may be pulled up as often as desired without disturbing the bulb E. The whole apparatus is surrounded by a large vacuum tube containing a paste of solid carbon dioxide and ether.

The heats of formation of the hydrobromic acid salts of methyl alcohol, acetone and ether were measured in this apparatus. The organic liquids unite with hydrogen bromide,

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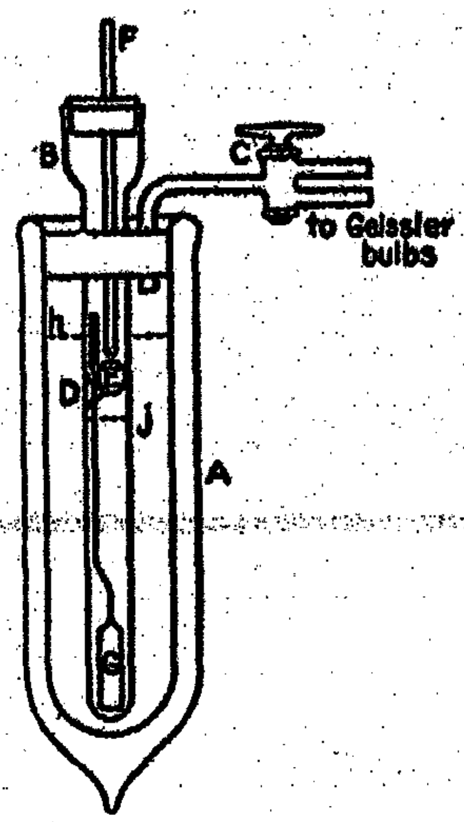
[1] Walker, McIntosh and Archibald: Jour. Chem. Soc., 85, 1098 (1904).

[2] Ibid., 85, 919 (1904).

giving the compounds $CH_3HO.HBr$,[1] $C_2H_6O.HBr$[2] and $C_4H_{10}O.HBr$. These additive bodies are white crystalline substances with low melting-points and dissolve in liquid hydrobromic acid with a heat evolution so small that it is difficult to measure. The heat of solution of a gram molecule of these hydrobromic acid salts is probably not larger than two or three kilojoules.



In performing an experiment A was filled with liquid hydrochloric acid (boiling-point —83°) to *h*, and B with hydrobromic acid (boiling-point —68°) to *j*. The bulb E containing a weighed quantity of the organic liquid was placed in position and all stoppers were tightly inserted. The stirring was begun and the amount of hydrochloric acid evaporated in a given time determined by the increase in weight of a Geissler bulb containing potash, the acid passing through mercury before being absorbed. (This evaporation of acid is referred to subsequently as "natural evaporation".) Then another Geissler tube was attached, the bulb E broken by the glass rod F and the liquid was stirred at the same rate as in

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[1] Jour. Am. Chem. Soc., 27, 26 (1905).

[2] Archibald and McIntosh: loc. cit.

the measurement of the "natural evaporation." The difference in the amounts of acid vaporized gave the evaporation due to the reaction, and from the latent heat of vaporization of hydrochloric acid (previous paper) the result is easily calculated in mechanical units. I might add that it is necessary to keep the vessel containing the organic liquid above the surface of the acid, and to mix slowly, for if the reaction be allowed to take place rapidly (with E at the bottom of the tube B) the pressure developed may become great enough to shatter the apparatus.

An example will make the method of calculation clear.

Heat of formation of methyl alcohol hydrobromide

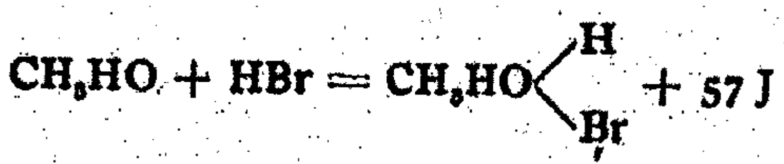
	Time in minutes	Evaporation	Rate per minute	Mean	Due to alcohol
Natural evaporation	5	0.170 g	0.0340		
Alcohol added 0.0770	8	0.637	—	0.0376	0.336
Natural evaporation	5	0.207	0.0412		
Alcohol added 0.1160	7	0.771	—	0.0406	0.487
Natural evaporation	7	0.235	0.0401		

In the first case 0.336 of a gram of hydrochloric acid is vaporized by the combination of 0.0770 of a gram of alcohol with hydrobromic acid. The heat of formation of a gram molecule of the sale is therefore

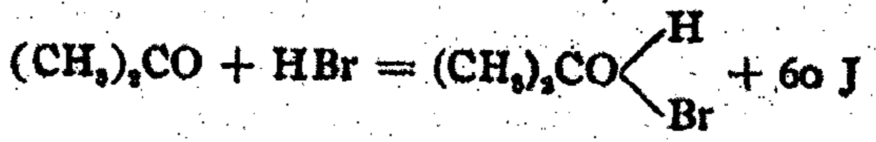
$$H = \frac{0.336 \times 32}{0.0770 \times 36.5} \times 14.8 \times 10^{10} \text{ ergs} = 56.6 \times 10^{10} \text{ ergs}.$$

The results are: Methyl alcohol: 56.6, 54.5, 59.3 × 10^{10} ergs.
Acetone: 56.5, 58.5, 60.9, 67 × 10^{10} "
Ether: 90.0, 83.2, 115.3 × 10^{10} "

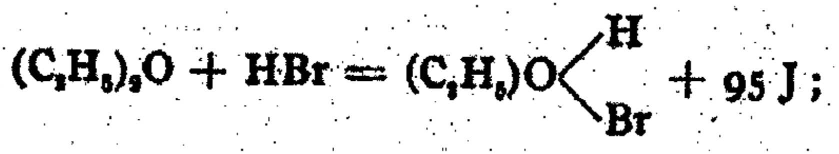
The agreement of the numbers is not wholly satisfactory, but as the carbon dioxide used is costly, I have not attempted to obtain more exact results. Moreover, an approximate value of the heats of formation is sufficient for any theoretical deductions that may be made. The figures are probably correct to 10 percent, and we may write



$$CH_3HO + HBr = CH_3HO\left\langle\begin{matrix}H\\ Br\end{matrix}\right. + 57\ J$$



$$(CH_3)_2CO + HBr = (CH_3)_2CO\left\langle\begin{matrix}H\\ Br\end{matrix}\right. + 60\ J$$



$$(C_2H_5)_2O + HBr = (C_2H_5)O\left\langle\begin{matrix}H\\ Br\end{matrix}\right. + 95\ J;$$

while the energy equation for the neutralization of potassium hydrate with hydrobromic acid is

$$\overset{+}{K}\overset{-}{OH} + \overset{+}{H}\overset{-}{Br} = \overset{+}{K}\overset{-}{Br} + H_2O + 57.3\ J.$$

The heat development in the experiments described above is large but many acids entering into solution give equally great amounts. Thus for hydrobromic acid we have

$$HBr + aq. = HBraq. + 100J.$$

In this case no compound is known to exist in solution and it may be urged that the heat evolved in the experiments described in this paper, is due merely to the heat of solution of the organic body in the acid That the compound formed dissolves with only a slight heat evolution does not affect this view, since Berthelot[1] has shown that during the solution of potassium hydroxide in water, nearly all the heat is developed in the formation of the hydrate $KOH2H_2O$, and that this body dissolves a slight heat absorption. However the additive products formed from the acids and organic oxygen compounds are so essentially different from the so-called molecular compounds—salts with water of crystallization—that I shall, for the present, regard the heat developed as due to the formation of compounds in which oxygen functions as a tetravalent element.

McGill University, Montreal.
December, 1907.

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[1] Ann. Chim. Phys. [5] 4, 513, 1875.

THE THREE-COMPONENT SYSTEM—CuO, SO_3, H_2O—AT 25°[1]

BY J. M. BELL AND W. C. TABER

In two previous papers[2] we have determined the composition of the solutions and of the solids resulting when lime is added in great excess to solutions of copper sulphate, and also when the sum of the bases present is exactly equivalent to the sulphuric acid. In the former paper it was found that at 25° the solid phases containing calcium were lime and gypsum, and that the solid phases containing copper were two modifications of copper hydroxide. The latter paper contained the mutual solubility relations of copper sulphate and calcium sulphate at 25°. When lime is added to a solution of copper sulphate in insufficient quantity to precipitate all the copper, the resulting precipitate at 25° is light green in color, and under the microscope was seen to consist of the well-known crystals of gypsum mixed with a green substance containing copper.

The composition of the green precipitate could not be determined on account of the quantity of calcium sulphate which was mixed with it. Where a base having a more soluble sulphate was employed, such as soda or potash, a precipitate was obtained having physical characteristics the same as that mixed with the gypsum. This precipitate was undoubtedly a basic sulphate of copper.

There have been recorded in the literature a number of basic sulphates of copper stable at ordinary temperatures. According to Sabatier,[3] many of the basic sulphates are not definite compounds, but more probably are mixtures. Brief reference will be made here to those which are said to exist under ordinary conditions of temperature and moisture.

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[1] Published by permission of the Secretary of Agriculture.

[2] Jour. Phys. Chem., 11, 632, 637 (1907).

[3] See Moissan: Traité de Chimie minérale, 5, 81 (1906).

Sabatier[1] prepared $5CuO.2SO_3.5H_2O$ by contact of another basic sulphate, $4CuO.SO_3.4H_2O$ with a saturated solution of copper sulphate. The former is green in color and is decomposed in cold water to the latter compound, copper sulphate passing into solution.

This latter basic sulphate of copper, $4CuO.SO_3.4H_2O$, *langite*, was prepared by Sabatier[1] by contact of copper oxide or hydroxide in the cold with solutions of copper sulphate containing less than 63 grains of copper per liter. It was also prepared by Pickering[2] by treating copper sulphate solution with ammonia, and by Kane[3] by treating with water the product formed by heating a compound of copper sulphate and ammonia ($CuSO_4.4NH_3.H_2O$). Langite is not changed in the air below 150° nor when treated with cold water.

André[4] has described the compound $4CuO.SO_3.16H_2O$, produced by saturating a hot ammonium sulphate solution with copper oxide and pouring the liquid into cold water.

Smith[5] has recorded the compound $6CuO.SO_3.6H_2O$, obtained by adding a slight excess of potash to a solution of copper sulphate.

Kane[6] formed the compound $8CuO.SO_3.12H_2O$ by precipitating copper from a solution of copper sulphate with alkali, stopping just short of the point where the solution becomes alkaline. The existence of this compound has been questioned by Smith.[5]

The present paper contains the results of experiments by treating various solutions of copper sulphate with copper oxide or copper hydroxide. The same final state was obtained regardless of the form in which the excess of copper oxide was added to the solutions. When ignited copper oxide was employed, a longer period of time was required for the attain-

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[1] Comptes rendus, 125, 101 (1897).

[2] Chem. News, 47, 181 (1883).

[3] Ann. Chim. Phys. [2], 72, 269 (1839).

[4] Comptes rendus, 100, 1138 (1885).

[5] Phil. Mag., 23, 496 (1843).

[6] Ann. Chim. Phys. [2], 72, 269 (1839).

ment of equilibrium conditions. The bottles containing the oxide were kept at 25° over two months, while those containing the hydroxide required only a few weeks to come to equilibrium. At the end of this time the solutions were analyzed for copper oxide and sulphuric anhydride; and also the precipitates freed as far as possible from the mother-liquor were analyzed. These compositions were plotted on a triangular diagram and the corresponding points joined by straight lines. In all the solutions copper and sulphuric acid were found in equivalent quantities, the net result being a loss from the solution of copper sulphate and possibly of water. The following table gives the results of the analyses.

No.	Liquid		Residue	
	Percent CuO	Density	Percent CuO	Percent SO_3
1	1.165	1.0192	33.96	9.75
2	2.18	1.0443	33.23	9.85
3	3.25	1.0672	33.27	10.43
4	4.30	1.0916	31.80	10.55
5	5.22	1.1103	31.58	11.01
6	6.21	1.1360	26.40	10.42
7	7.14	1.1559	27.23	11.07
8	7.99	1.1745	27.92	11.63
9	8.72	1.2009	26.42	11.88

In the accompanying diagram the lines joining the points on the curve AD to the corresponding points representing the compositions of the residues do not meet within the triangle, although they tend to converge. This indicates that the solid phases consist of a series of solid solutions consisting of copper oxide, sulphur dioxide and possibly water. Thus there is no definite basic compound at this temperature. It will be observed that all the lines pass between the points marked M and N on the diagram, which points represent the compositions of the two basic sulphates which have the best status in the literature, *viz.*, $5CuO.2SO_3.5H_2O$ and $4CuO.SO_3.4H_2O$. The points representing the formulas $4CuO.SO_3.16H_2O$

and $6CuO.SO_3.6H_2O$, cited above, both lie near the area through which the lines pass.

In a paper recently published by Pickering[1] it has been shown that when just enough alkali is added to a solution of copper sulphate, the precipitate contains four equivalents of copper oxide to one equivalent of sulphuric anhydride, or $4CuO.SO_3$. This agrees well with the composition of the limiting solid solution in equilibrium with water, which solid solution is represented by a point on the line AP of the diagram. The ratio of copper oxide to sulphuric anhydride at any point on this line is equal to the ratio CP : BP, which is very nearly 4 : 1.

The range of solutions which exist in equilibrium with the solid solutions is from pure water on the one hand to a solution saturated with copper sulphate on the other. Unfortunately, the bottle containing both the limiting solid solution and solid copper sulphate was broken in the thermostat. It is certain, however, that the composition of the limiting solution would have been found to be the same as the solution saturated with copper sulphate in the absence of any of the solid solution, because copper and sulphuric acid in the solutions were always in equivalent proportions.

It is impossible from the data in hand to give the composition of the solid solutions, which would be represented by a line between points on the limiting straight lines below the points representing the composition of the residues.

The other possible solutions in the three component system—copper oxide, sulphuric anhydride, water—are obtained when the total acid is in excess of the copper oxide. The solubility of copper sulphate in sulphuric acid solutions at 0° has been determined by Engel,[2] who considers that there is a definite combination of sulphuric acid and water, the rest of the water present dissolving copper sulphate as if no acid were present. In the present experiments copper sulphate was added to different aqueous solutions of sulphuric

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[1] Jour. Chem. Soc., 91, 1981 (1907).

[2] Comptes rendus, 104, 506 (1887).

acid. After two weeks constant agitation in the thermostat at 25°, the solutions were analyzed and also the solid phase with adhering mother-liquor. The results have been plotted in the accompanying figure, and it will be seen that over a certain range the lines joining the corresponding points pass through the point representing the composition $CuSO_4.5H_2O$. At greater concentrations of sulphuric acid there is a range of solutions in which the tri-hydrate ($CuSO_4.3H_2O$) is stable, and at still higher concentrations the monohydrate ($CuSO_4.H_2O$) is stable. Finally, a solution was obtained in which the anhydrous salt was the stable solid phase.

The following table gives the results of the analytical data:

Solution			Residue		Solid phases
Density	Percent CuO	Percent SO_3	Percent CuO	Percent SO_3	
1.2142	9.17	9.26	30.24	30.35	$CuSO_4.5H_2O$
1.2248	5.91	15.90	30.62	31.30	$CuSO_4.5H_2O$
1.2593	3.39	23.09	29.11	31.08	$CuSO_4.5H_2O$
1.2934	1.82	28.75	31.15	31.70	$CuSO_4.5H_2O$
1.4061	1.32	39.74	30.34	32.08	$CuSO_4.5H_2O$
1.4256	—	41.29	29.81	35.26	$CuSO_4.5H_2O$; $CuSO_4.3H_2O$
1.4249	—	41.04	27.4	38.47	$CuSO_4.3H_2O$
1.4516	1.38	43.63	32.65	38.29	$CuSO_4.3H_2O$
1.4915	1.02	47.82	32.77	38.70	$CuSO_4.3H_2O$
1.5124	—	49.07	20.16	47.54	$CuSO_4.H_2O$
1.5408	0.38	51.46	30.42	46.89	$CuSO_4.H_2O$
1.5643	0.368	53.51	26.34	48.73	$CuSO_4.H_2O$
1.6824	0.109	62.14	26.46	51.76	$CuSO_4.H_2O$
1.7752	0.105	68.34	31.82	51.82	$CuSO_4.H_2O$
1.8118	0.15	72.41	30.50	54.12	$CuSO_4.H_2O$
1.8266	0.07	74.26	30.50	59.70	$CuSO_4$

Besides the above hydrates, Graham[1] has recorded the compound $CuSO_4.2H_2O$, obtained by confining the pentahydrate in a dry space for a week at 20°. From his study of the vapor tensions of the hydrates of copper sulphate,

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[1] Phil. Mag., 6, 419 (1835).

Lescoeur[1] concludes that a compound of this composition does not exist, and from the solubility determinations of the present paper no evidence was obtained for the existence of this compound. Two other hydrates, $CuSO_4.6H_2O$ and $CuSO_4.7H_2O$, have been recorded by Lecoq de Boisbaudran.[2] These were obtained by adding a small crystal of nickel sulphate ($NiSO_4.6H_2O$) or of ferrous sulphate ($FeSO_4.7H_2O$) to a supersaturated solution of copper sulphate. Crystals isomorphous with those salts separated but were metastable; copper sulphate pentahydrate, the stable solid phase, soon separated from the solutions and the higher hydrates disappeared.

From his work on the relative vapor pressures of copper sulphate crystals in various stages of dehydration, Andreae[3] concludes that there exist only the pentahydrate, trihydrate and monohydrate.

The figure shows that the solubility of copper sulphate is depressed upon the addition of sulphuric acid, for from D to E the curve approaches the side AC of the triangle. Between the points D and E the lines joining the corresponding points for solution and residue all meet in the point 5, which represents the composition $CuSO_4.5H_2O$; from E to F the corresponding lines meet in the point 3, which represents the composition $CuSO_4.3H_2O$; from F to G the corresponding lines meet in the point 1, which represents the composition $CuSO_4.H_2O$. Beyond the point G, only one line was determined and this line passes through the point O, representing the composition $CuSO_4$. Undoubtedly the solid phase is anhydrous copper sulphate, although this can not be affirmed from the data at hand, for by this method of representation, it is necessary to have at least three lines meeting at a point before the existence of a compound is definitely established.

The quantity of copper oxide in solution is very small for

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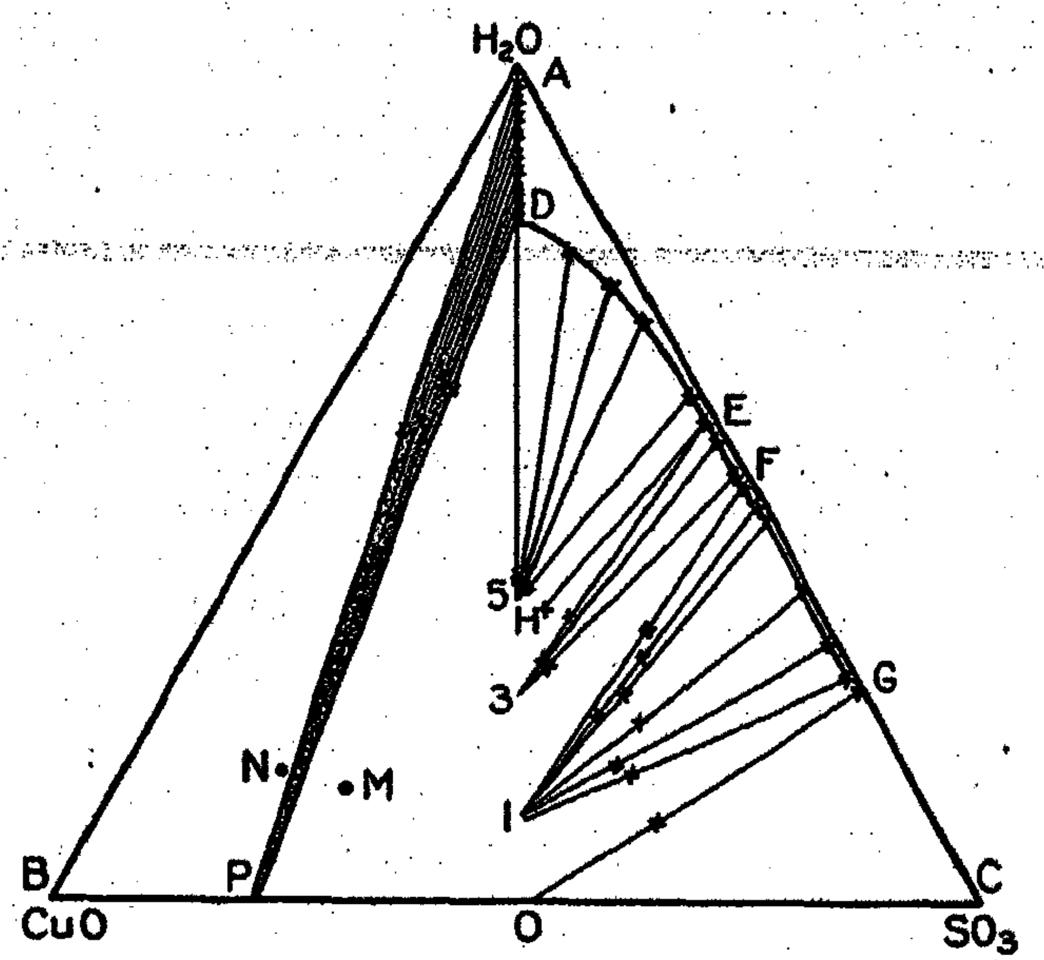
[1] Bull. Soc. chim. Paris, [2], 46, 285 (1886); Comptes rendus, 102, 1466 (1886); Ann. Chim. Phys. [6], 21, 544 (1890).

[2] Comptes rendus, 65, 1249 (1867); 66, 497 (1868).

[3] Zeit. phys. Chem., 7, 260 (1891).

the greater quantities of sulphuric acid, and at the point E there is less than 2 percent copper oxide to 41.29 percent of sulphuric trioxide in solution; at the point F still less copper is in solution, and at G only a very small amount.

The straight line EH which passes through E does not pass through the point 5 or the point 3, but passes between them. This is due to the fact that at E two solid phases are present, the dark blue copper sulphate pentahydrate and lighter copper sulphate trihydrate, both of which could be easily seen in the residue. The exact position of the point F has not been definitely determined, although it may be stated from the data the percentage of sulphuric acid lies between 47.8 and 49.1; also the exact determination of the point marked G was not made, the solution at this point being very concentrated with respect to sulphuric acid.



The transformation represented by the equation

$$CuSO_4.5H_2O \rightleftarrows CuSO_4.3H_2O + 2H_2O$$

takes place under certain well-defined conditions; and conversely the coexistence of the two hydrates is possible only under certain well-defined conditions. Lescoeur[1] has determined the vapor pressure at different temperatures at which the two hydrates coexist; at 25° this vapor pressure was 8.5 mm. Frowein,[2] also, has made similar determinations and, by extrapolation, the value 7.2 mm was found as the vapor pressure at 25°. The present data show that this transformation takes place in a solution containing 41.29 percent SO_3 and 1.42 percent CuO. Neglecting the small influence of the small quantity of copper oxide upon the vapor pressure, the vapor pressure of a solution containing 41.29 percent SO_3 was computed as 8.60 mm at 25° from the results of Sorel;[3] as 8.48 mm from the data of Regnault;[4] and as 8.45 mm from the data of Richards.[5] These values agree well with the values for the vapor pressure at which this transformation takes place as found directly by Lescoeur. Thus the vapor pressure data and the solubility data agree in a satisfactory manner.

Again, the transformation represented by the scheme

$$CuSO_4.3H_2O \rightleftarrows CuSO_4.H_2O + 2H_2O$$

takes place at a definite vapor pressure for each temperature. Extrapolating from the results of Lescoeur at slightly higher temperature, the value 3.2 mm was found. Again neglecting the small influence of the copper oxide present at the point F, and computing from the available measurements, the vapor pressure of a solution containing 48.5 percent SO_3, which is very close to the composition of the solution at F, the value 4.5 mm was obtained. The lack of agreement may be ascribed to the fact that Lescoeur's determinations are recorded in whole numbers of millimeters and in halves of millimeters and are therefore correct only to half a millimeter. Further, the value 3.2 mm is an extrapolated value, the lowest measurements made being 5 mm at 30°, and 7.5 mm at 35°. Conse-

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[1] Loc. cit.

[2] Zeit. phys. Chem., 1, 1 (1887).

[3] Zeit. angew. Chem., 1, 272 (1889).

[4] Ann. Chim. Phys. [3], 15, 179 (1845)

[5] Proc. Am. Acad., 33, 23 (1897–98).

quently the error in the value taken, 3.2 mm, is probably very great.

From what has been presented above it follows that:

(1) There is at 25° no definite basic sulphate of copper, all the basic sulphates being solid solutions, as is shown by the fact that the lines in the accompanying diagram do not meet within the triangle. The solutions in contact with these basic sulphates contain sulphuric anhydride and copper oxide in equivalent quantities, and are all slightly acid in reaction.

(2) At 25° the following hydrates of copper sulphate are stable: $CuSO_4.5H_2O$ between the vapor pressure of water at this temperature and 8.5 mm; $CuSO_4.3H_2O$ between vapor pressures of 8.5 mm and 4.5 mm approximately; $CuSO_4.H_2O$ between the latter value and a very low vapor pressure, probably about 0.1 mm. The anhydrous salt $CuSO_4$ is stable below this last vapor pressure.

Bureau of Soils,
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Washington, D. C.

THE ELECTROLYTIC CORROSION OF THE COPPER-ALUMINUM ALLOYS

BY W. S. ROWLAND

B. E. Curry[1] has determined the constitution of the aluminum bronzes. He has shown that on annealing to equilibrium at 500°, the alloy from pure copper to pure aluminum consists of five phases. The five phases are four solid solutions and one compound $CuAl_2$, as appears from the concentration-temperature diagram, Fig. 1.

From 100 percent to 91 percent copper there exists the α phase; from 91 percent to 84 percent copper a mixture of the α and γ phases; from 84 percent to 79.5 percent pure γ; from 79.5 percent to 75.5 percent γ and ε; from 75.5 percent to 73 percent ε; from 73 percent to 54 percent a mixture of ε and the compound $CuAl_2$; from 54 percent to 10.75 percent $CuAl_2$ and η; and from 10.75 percent to 0 percent copper the pure η phase.

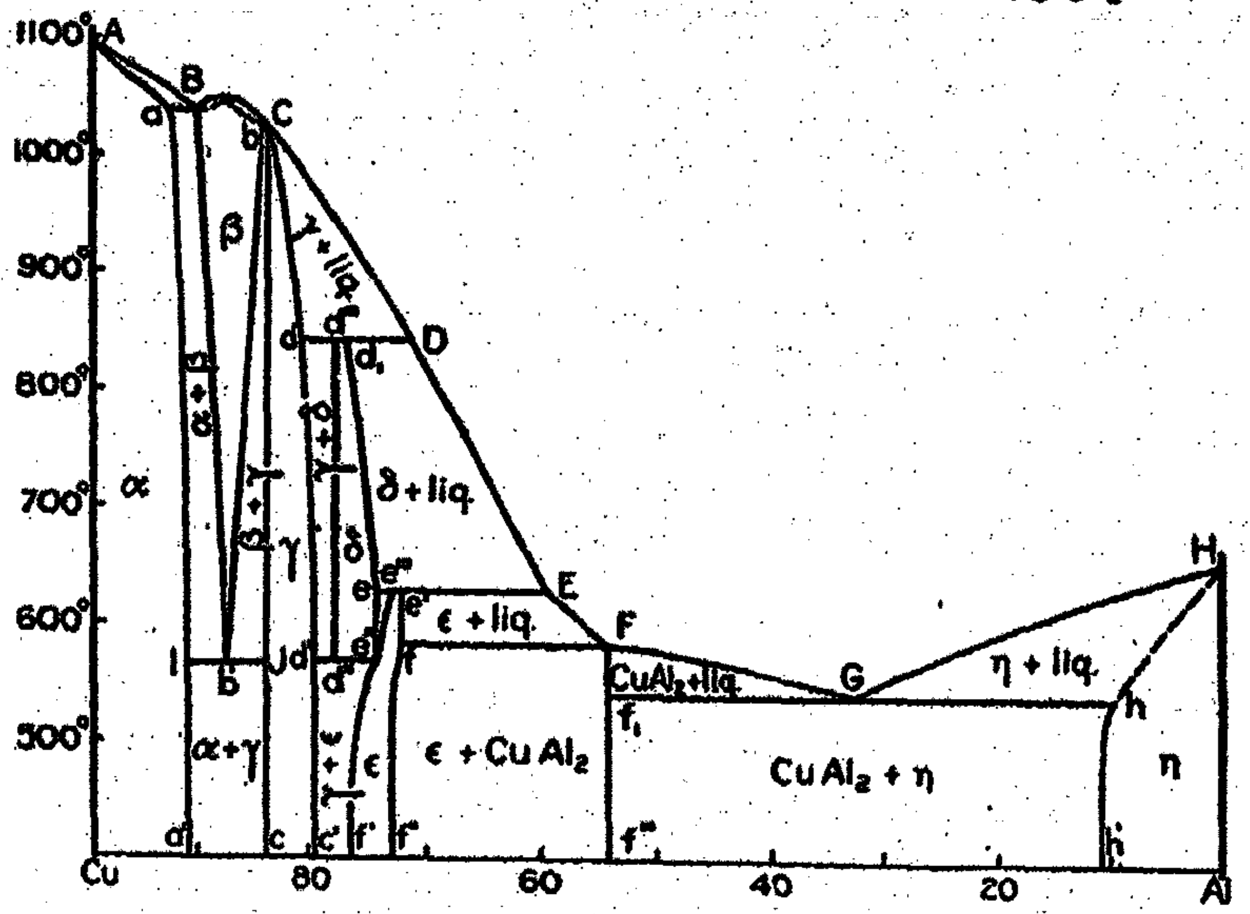

Fig. 1

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[1] Jour. Phys. Chem., 11, 425 (1907).

Annealed to 610°, the α phase exists from 100 percent copper to 91 percent. From 91 percent to 87.5 percent there is a mixture of the α and β phases, and from 87.5 percent to 84 percent the field is made up of the β and the γ phases. Below 84 percent the γ phase exists alone until 79.5 percent copper is reached.

Up to the present time very little has been done in commercial practice with these bronzes. They have remarkably fine properties in some percents of copper but the practical metallurgists seem to be very slow in taking advantage of them. This is partly due to the great variety of physical properties which are met with in the varying percents of copper, owing to the changes in the nature of the phases. Certain alloys are extremely brittle, almost crumbly, so that it requires the greatest care in handling them. Other alloys are extremely tough. Throughout the field the greatest variety of ductility can be obtained.

In a paper on the tensile strengths of the aluminum bronzes B. E. Curry[1] has given some very interesting data on the physical properties of the alloys.

Another difficulty up to the present time which seems to stand in the way of commercial work with the copper-aluminum alloy, has been in the casting, but it would seem that if the proper kind of moulds were used and care be taken not to "burn" the metal, little trouble should be encountered.

In the following pages it is hoped that some idea may be given of the relative solubility of the different phases of the aluminum bronzes in solutions of some of the more common sodium salts.

At first it was intended to make corrosions with the following percents of copper, 5, 10, 15, 25, 35, 45, 50, 55, 60, 65, 73, 79, 84, 85, 87, 88, 89, 90, 91 and 96, annealed at 500°, but as the work progressed it was found necessary to run other percents than those mentioned above in order more clearly to describe the corrosion of the various phases.

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[1] Curry and Woods: Jour. Phys. Chem., 11, 461 (1907).

Alloys with 84, 85, 87, 88, 89 and 90 percent of copper were annealed at 610° to show the comparative corrosion in the $\alpha + \beta$ and $\beta + \gamma$ fields. It was found impossible to quench alloys below 83 percent of copper from 610° on account of the great brittleness of the γ phase and therefore corrosion of pieces, annealed at 610° and containing less than 83 percent copper, had to be omitted.

The alloys were made of electrolytic copper and 99.99 percent aluminum.[1] An ordinary gas blast furnace was used. The crucibles were made from Acheson graphite. Up to about 50 percent the aluminum was first melted under powdered carbon and the copper then added. With higher percents of copper, the copper was melted first. Powdered graphite was kept upon the surface of the melt. The castings were made in graphite moulds containing places for about five test pieces. Usually about 12 pieces were made from each cast. Working with graphite moulds and crucibles kept the alloy from contamination and there was seldom any difficulty experienced in getting clean and homogeneous castings. The crucibles were made by boring out a solid rod of graphite, about five inches in diameter, leaving a wall about one-half inch in thickness and a base of about three inches in height. This solid base allowed the blast to heat the crucible in a very satisfactory manner, without being driven directly against the walls, and thus considerably prolonged its life.

In the annealing, a nickel wire resistance furnace was used in which the temperature could be maintained very accurately at the degree desired by means of varying external resistance. At 610° about two hours time was sufficient to bring the phases to equilibrium. These pieces were quenched from that temperature in ice water. The pieces annealed at 500° were held at that temperature for five hours after repeated trials. It was found impossible to quench alloys of from 84 percent to 54 percent copper, and keep them from

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[1] Presented by Aluminum Co. of America.

breaking, either as they were being quenched or as they were being cleaned. The γ and ϵ and the pure $CuAl_2$ phases are extremely brittle and test pieces containing these crystals can easily be fractured with a slight blow. Test pieces with the above percents of copper were therefore slow-cooled in the furnace after which they could be handled fairly satisfactorily, although still very brittle.

Curry's diagram does not cover temperatures below 400° but it is doubtful if any phase changes take place below that temperature and therefore slow-cooling from 500° probably answers the purpose. The work had to be done in this way or the corrosions from 54 percent to 84 percent copper omitted altogether.

Pieces containing from 100 percent to 84 percent and from 54 percent to 0 percent were quenched from 500°.

After annealing, the test pieces were cleaned on a carborundum wheel, care being taken to remove all oxide films. If necessary, they were afterwards smoothed off with a carborundum paper.

The test pieces were about 8 cm long and 0.8 cm in diameter. They were rotated during the corrosion at a rate sufficiently rapid to prevent any hydroxide film from adhering to them. This was accomplished by using small Ajax motor frames, so arranged that they could be rotated uniformly from a main shaft, which in turn was belted to a motor. The test pieces were attached to the motor shafts by binding posts. Each machine held five test pieces.

Later a machine was devised along the above lines and built by Messrs. Thomas and Grant, of Ithaca, N. Y. The whole apparatus was made heavier and more stable, and is arranged so that the speed may be varied. It is driven by a Westinghouse A. C. fan motor. As with the first machine used, the five sets are wired in series, but each set has a two-way switch attached so that any one of them may be cut out of the series without interrupting the current in the others. This was found of great convenience in cases where any one test piece became aluic[1] and had to be cut out of the circuit.

A current of 35 milamperes was passed through the solutions for from seven to nine hours. At first an attempt was made to maintain the current constant throughout the entire time so that on each corrosion 280 milamp. hours would be used, but this was found very difficult to accomplish and therefore the 280 milamp. hours was in most cases only approximated. This is in reality of little moment for all the efficiency calculations are based upon the gain in weight of the cathode in a copper coulometer solution which is assumed to have 100 percent current efficiency.

The current efficiency curves which follow were obtained in the following manner with the one exception as noted under the corrosion in the sodium sulphate solution. A copper coulometer solution with copper electrodes was placed in series with each set of corrosions. The gain in weight of the cathode was taken as representing 100 percent current efficiency, and the efficiencies of the corrosions with the various percentage test pieces were obtained by using an electrolytic equivalent for each particular percentage and comparing it with the cathode coulometer gain. In these calculations aluminum was taken as trivalent while copper was made bivalent, except in the NaCl solution where it was taken as univalent, for it is well known that in chloride solutions copper dissolves in the cuprous form.

Inasmuch as in practically every case where there is the formation of hydroxides which are precipitated, there is a

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[1] Up to the present the word "passive" has been used to signify a condition such that a metal as anode did not dissolve, even although the current continued to flow. A case of this is that of iron going passive in concentric nitric acid. The term has also been applied to an aluminum anode in a sulphuric acid solution but here the aluminum not only does not dissolve but also, by the formation of an oxide film, prevents the further flow of the current. To differentiate between these two conditions the word aluic will be used for the second case, that is, where the metal neither dissolves nor allows the passage of a current. Aluic is from the Greek word λύω meaning to flow, with the α signifying the negative, that is, non-flowing.

certain amount of acid occluded in the precipitate, there was a tendency in all such instances for the solution to turn alkaline at some time during the run.[1] Theoretically, in a case for instance, where there is little solution taking place at the anode, there is formed at that electrode free acid, as

$$SO_4 + H_2O = H_2SO_4 + O$$

and at the cathode, in a Na_2SO_4 solution,

$$2Na + 2H_2O = 2NaOH + H_2$$

and then as the acid and the base diffuse through the solution they again unite to neutralize each other. But with the electrolysis of a solution which attacks the anode, the NaOH from the cathode precipitates the hydroxide of the metal dissolved and there is a certain amount of the acid radical occluded in this precipitate. This of course leaves a certain amount of free base for which there is no acid radical, with the result that the solution becomes alkaline.

Looking ahead to Table 1 of the corrosion in NaOH it will be seen that both the $CuAl_2$ and the η phases are soluble, and therefore the values for the corrosion of those phases may be raised very considerably in the cases where the solutions have turned alkaline. The amount of solution in the sodium hydroxide depends of course upon its concentration which in turn depends upon the amount of acid occluded in the hydroxides precipitated. It further depends upon the time of the run, the speed of rotation, etc., etc., and as it was impossible to keep these factors absolutely constant, the points obtained in the efficiency curves below 73 percent copper cannot be absolutely comparable. It was deemed wise, however, to draw the curves as best possible with the data obtained, and in some cases dotted lines have been drawn to show the direction of the actual current efficiency values.

The corrosions were done in heavy beakers, containing about 200 cc of the solution. Platinum wire was used for the cathodes.

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[1] Cf. Pickering: Jour. Chem. Soc., 91, 1981 (1907).

Corrosions of pieces annealed at 500° were done in the following solutions: 7 percent NaOH, 7 percent Na_2SO_4, 7 percent NaCl, 7 percent $NaNO_3$, 7 percent Na_2CO_3, 7 percent CH_3COONa, 3 percent $(COO)_2Na_2$ + 3 percent $(COOH)_2$, and 7 percent $C_4H_4O_6Na_2$ + 3 percent NaOH. Corrosions of pieces annealed at 610° were done in the chloride, sulphate and nitrate solutions.[1]

After the run the test pieces were removed and cleaned of any adherent oxide or film. This was accomplished by a few minutes work with a rubber-tipped glass rod. In certain cases it was found very difficult to remove all of the oxides without also scraping off some of the uncorroded portions.

In cases where there were non-removable oxides left on the test piece or where the finely divided copper which was left on a copper-rich surface had been oxidized by the air, reduction was effected by heating the pieces in a combustion tube through which a stream of hydrogen was passed.

With test pieces containing two phases, one of which is present in greater proportion than the other (and this, of course, occurs on the border of certain fields), and where one phase is soluble and the other insoluble or comparatively so, there is apt to be a solution of the more soluble phase such that it is completely dissolved from around the other phase and then that less soluble phase is mechanically dislodged from the test piece by the rotating motion. In this case one of two things may happen. The dislodged crystals may remain undissolved in the bottom of the beaker or they may after a time go into solution by chemical action independent of the electrolysis. Further, if they are dissolved, they may go into solution either quantitatively, or the copper or the aluminum be dissolved out and the remainder, being left in a very finely divided state, may be precipitated as the hydroxide, if the solution has turned alkaline during the run. This "falling off" tendency is most apt to take place near

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[1] The greater part of the corrosions in the chloride, sulphate, nitrate and hydroxide solutions were made by R. B. Roe.

the edge of a field, and unless care is taken in the work, it may cause results which are higher than the actual efficiency values.

When the efficiency values run over 100 percent there is evidence of one of three things having happened. Either there has been a "falling off" of a relatively insoluble phase, or there has been chemical action upon the test piece in addition to that produced by the electrolysis, or possibly the copper or aluminum or both are dissolving with some valence lower than that upon which the efficiency is being calculated. It is very unlikely that this last case would occur. Unfortunately, with all percents of copper below 73 percent, and "falling off" could not be detected unless it were the ϵ phase, for both the $CuAl_2$ and the η phases are soluble in the alkaline solution, which is in most cases formed when there are hydroxides precipitated.

As a matter of experiment no cases were noted where there was any apparent dislodgement of crystals, except in some of the most brittle alloys and here it was due more to their crumbly nature. The runs in these cases were repeated and if the second time unsuccessful the data were omitted.

Any deposit on the platinum cathode was dissolved in nitric acid upon completion of the run and the whole solution made slightly acid with HNO_3 and H_2SO_4. These solutions were then electrolyzed, the copper being deposited upon rotating platinum electrodes. The machine which was used for the corrosion was also used for the analyses. With the solutions of the organic compounds, it was found very difficult to get good deposits from acid solutions. It was found necessary first to deposit the copper from an ammoniacal solution and then to redissolve in and redeposit from a nitric-sulphuric acid solution. In this way very good deposits were obtained.

During the runs the presence of precipitates, oxide films, cathode deposits, etc., etc., was carefully noted and this was found of great use in explaining certain of the data which appeared abnormal.

Electrolytic Corrosion in Sodium Hydroxide Solution

In Table 1 are given the data obtained from the corrosion in a 7 percent solution of NaOH. The first column represents the percent of copper in the test piece, the second the corrosion in grams, which is obtained by weighing the test piece before and after the corrosion. The third column contains the amounts of copper corroded including that, if any, which was deposited upon the cathode, and the fourth column contains the percentage of copper dissolved to the total corrosion.

TABLE 1

Corrosion in 7 percent sodium hydroxide solution

Percent of Cu in test piece	Corrosion in gram	Copper corroded in gram	Percent of copper corroded
0.0	0.1855	0	0
4.5	0.2439	0.0089	3.64
10.0	0.2168	0.0161	7.43
15.1	0.2862	0.0382	13.32
25.0	0.2406	0.0473	19.66
35.2	0.2873	0.0816	28.40
45.6	0.3739	0.1446	38.67
50.5	0.3410	0.1149	33.69
51.9	0.3526	0.1138	32.27
58.8	0.0920	trace	—
72.3	0.0062	0.0013	—
74.3	0.0053	0.0022	—
77.2	0.0050	0.0025	—
83.6	0.0063	0.0023	—
84.2	0.0020	0.0007	—
86.4	0.0019	0.0007	—
87.4	0.0016	0.0010	—
89.5	0.0019	0.0010	—
90.1	0.0022	0.0016	—
96.0	0.0031	0.0023	—

The principle item of note in this corrosion is the fact that the η and the $CuAl_2$ phases are the only ones which dissolve in NaOH. The corrosion practically reaches a maximum at 54 percent copper, where $CuAl_2$ exists alone. With the introduction of the ϵ phase it drops off very considerably and from then on through the higher percents of copper the corrosion is practically zero.

From the fact that no copper is obtained from the corrosion in the $\epsilon + CuAl_2$ field, it would appear that the copper corroded comes entirely from the η phase, and yet the percentage of copper to the total corrosion increases with the amount of copper in the test piece. This makes it impossible for the copper to come entirely from the η phase for two reasons. First the η phase has only 10.75 percent of copper in it throughout the $CuAl_2 + \eta$ field and say in a 52 percent test piece, there would not be enough copper in the η phase present at that percent to furnish 32 percent of copper in the entire amount corroded, which is the result obtained experimentally. Secondly to have the percentage of copper in the solution constantly increasing across a field consisting of two phases where each has a constant composition but vary in ratio to each other, the phase from which the copper is dissolved must be the one which is constantly increasing. The amount of this last phase dissolved will also increase proportionately to the increase in copper in the test piece. The test piece would then be copper-rich at the end of the run while all the test pieces from 4.5 percent to 58.8 percent were corroded copper-rich in the sodium hydroxide solution.

It seems then that the copper must come from the $CuAl_2$ phase although no copper was obtained from that phase in the field of $\epsilon + CuAl_2$. The only explanation is that the presence of the η phase permits the solution of the $CuAl_2$ from which the copper must have come.

The fact that only the $CuAl_2$ and η phases are soluble in $NaOH$ gives considerable acid in explaining the data obtained in the corrosion of the bronzes by the alkaline tartrate solution and also in other solutions where the occlusion of acid by the precipitated hydroxides caused the solutions to go alkaline during the run.

There was no coulometer solution run in series with these corrosions and therefore no current efficiency curves can be drawn.

Electrolytic Corrosion in Sodium Sulphate Solution

The curves shown in Figs. 2 and 3 represent the current efficiency of the corrosion of the bronzes obtained by two different methods of calculation. The data from which these efficiencies are calculated is given in Table 2.

In this table, as in all following tables, with one omission mentioned later on, the first column represents the percent of copper in the test piece corroded. The second column gives the corrosion in grams and the third column contains the gain in weight of the cathode in the coulometer solution upon which, taken as 100 percent, is based the efficiency of the corrosion. The next two columns give the efficiencies as described in the following paragraphs. The sixth column gives the amount of copper in the solution after the corrosion together with that, if any, which was deposited on the cathode, and the last column gives the percent of copper to the total corrosion.

TABLE 2

Corrosion in 7 percent sodium sulphate solution

Percentage copper in test piece	Corrosion in gram	Coulom. cathode gain in gram	Percent efficiency by composition of test piece	Percent efficiency by analysis of solution	Copper corroded in gram	Percent of copper corroded
10.0	0.0451	0.3453	36.74	26.99	0.0125	27.71
15.1	0.0408	0.3453	29.76	24.31	0.0114	27.94
25.0	0.0364	0.3453	22.72	20.01	0.0123	33.79
35.2	0.0352	0.3149	20.78	20.07	0.0134	38.08
45.6	0.0401	0.3149	20.84	22.26	0.0161	40.14
55.0	0.0430	0.3023	20.95	24.03	0.0196	43.00
65.4	0.0703	0.3068	30.00	31.30	0.0460	63.00
72.3	0.1334	0.3337	49.78	51.39	0.0908	68.08
74.8	0.1200	0.3068	45.9	50.00	0.0892	74.30
76.0	0.1082	0.2638	49.47	56.55	0.0667	61.70
78.9	0.1210	0.2661	53.43	59.28	0.0815	67.30
80.0	0.0854	0.2213	45.00	46.21	0.0660	77.28
83.6	0.1877	0.3480	61.09	61.71	0.1545	82.31
84.2	0.2945	0.3888	85.49	84.35	0.2523	85.67
86.4	0.3154	0.3888	89.83	90.04	0.2713	86.01
89.5	0.3209	0.3888	89.13	89.94	0.2884	89.87
90.1	0.2933	0.3480	90.53	90.04	0.2658	90.62
96.0	0.3426	0.3480	103.0	102.9	0.3220	94.0

Fig. 2 represents the efficiency as calculated similarly to the remaining efficiency curves shown in this paper and previously described. While this curve represents the change in the corrosion with the changes in the phases, it is based upon the percentage of copper in the alloy involved. That is to say an electrochemical equivalent has been calculated in each case for each percentage. In Fig. 3 the electrochemical equivalent is calculated from the percentage of copper in the solution and on the cathode at the end of the run.

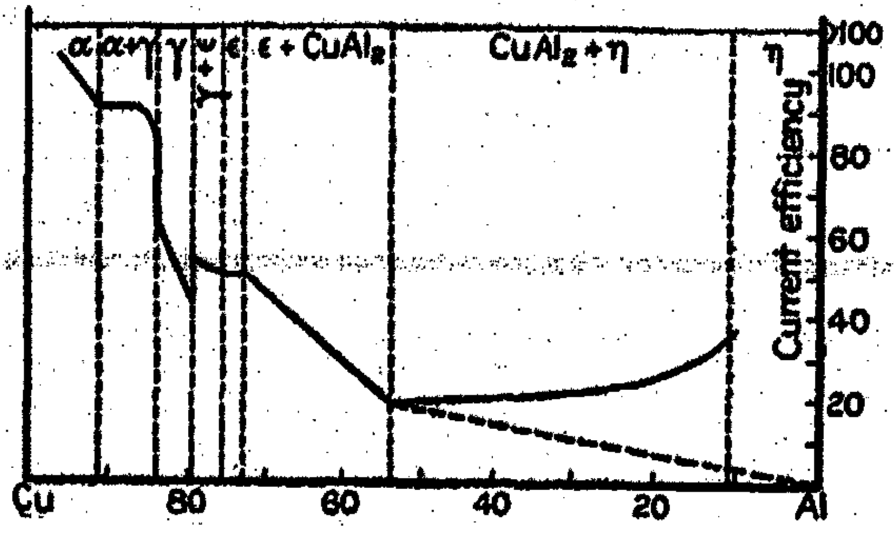

Fig. 2—Sodium sulphate solution

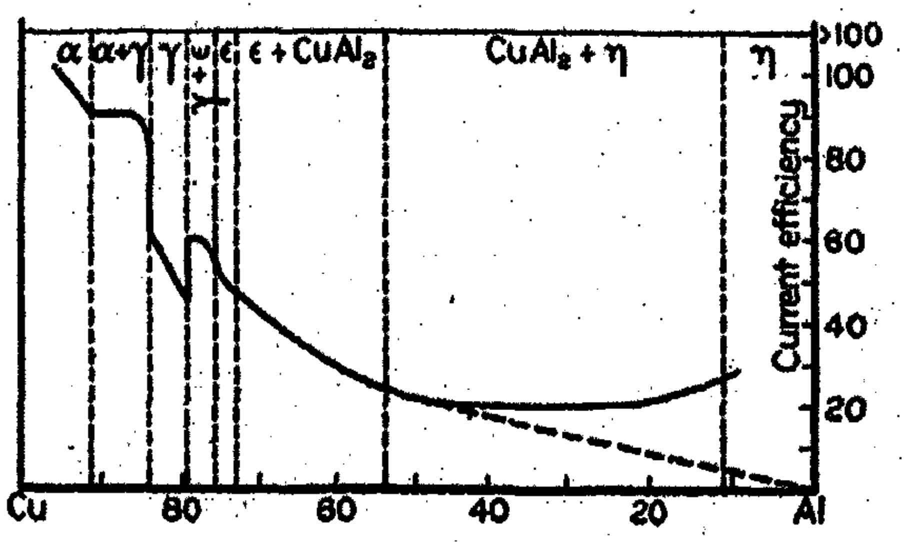

Fig. 3—Sodium sulphate solution

Both curves have practically the same turning points. It so happened that the percents of copper to the total corrosion held a fairly constant relation to the actual percentage of copper in the test piece corroded and only where there is a marked variation in the two percents, will the curves vary.

While in reality the current efficiency curves should be based upon the composition of the solution after corrosion, which is, of course, the composition of that part of the alloy which is dissolved, it would be difficult to get the correct efficiencies by this method due to the variations in the percents of copper corroded to the total corrosion. For this reason the curves which follow are obtained upon the basis of the actual composition of the alloy. The data for the other calculation are given and the efficiencies may be calculated if desired.

In the sulphate solution, Fig. 2, the α phase is the most soluble, with a decreasing efficiency with the decrease in its percent of copper. The efficiency gradually falls through the $\alpha + \gamma$ field with the disappearance of the α phase. With pure γ it is 60 percent. It continues to fall with the decreasing amount of copper in the γ phase.

The alloy dissolves almost according to its composition through the α, $\alpha + \gamma$ and γ fields. The appearance of the ϵ phase increases the efficiency, it being more soluble than the γ. It might be expected that changing on to pure γ might still further increase the efficiency, but in reality it drops off. This is probably due to the increasing aluminum content through the pure ϵ field.

The fact that the ϵ phase dissolves slightly copper-rich tends to increase the efficiency when based upon the analysis of the solution after corrosion. This is the only place where the two curves differ materially and here the difference is small.

Whenever there is the formation and precipitation of hydroxides, this is accompanied by the occlusion of acid, as explained before and the consequent formation of an alkaline solution with the NaOH produced at the cathode. In the NaOH both the $CuAl_2$ and η phases are soluble, the pure η probably more so than the pure $CuAl_2$ and for some reason not yet determined, the mixture of the two is more soluble than either. It is therefore impossible to do much more than to plot the results obtained and to state that the percents of copper in the solutions are influenced by the chemical corrosion of the sodium hydroxide as well as by the solution by the acid ion. However, it is made quite certain, by a comparison with Table 1 for the NaOH, that there is a solution of the $CuAl_2$ phase and also possibly of the η phase from the $CuAl_2 + \eta$ field in the sulphate solution. The high percents of copper obtained in the solution from the corrosion of the 10 percent, 15 percent and 25 percent copper pieces shows that the $CuAl_2$ must form the major part of the dissolved portion, and it is problematical as to whether the η phase is dissolved in the sulphate solution. Its solution in these runs may have been entirely due to action of the unneutralized NaOH.

At 45 percent the curve begins to decline less rapidly and at 35 percent reaches a minimum. From then on to the 10 percent composition in the η field it continues to rise, but it was impossible to any data on a 5 percent piece as it became aluic and no current could be sent through. The true electrolytic efficiency curve, if the alkalinity had been avoided, would probably go as indicated by the dotted line, running down to 0 percent with pure aluminum.

Electrolytic Corrosion in Sodium Nitrate Solution

Table 3 and Fig. 4 show the data and efficiency curve for the corrosion of the aluminum bronzes in a 7 percent solution of sodium nitrate. The α phase has the greatest solubility. This decreases slightly with the decrease in the amount of copper present. The γ and ε phases are considerably less soluble as shown by the rapid drop in the efficiency across the γ and the $\gamma + \varepsilon$ fields. With the disappearance of the γ phase, the efficiency rises slightly and remains almost constant across the $\varepsilon + CuAl_2$ field. Here the efficiency values first curve downward, reaching a minimum at 35 percent copper and then rapidly rise to 95 percent efficiency with the 5 percent copper. As in other cases, the great increase in the efficiency is largely due to the chemical corrosion of the NaOH after the solution has gone alkaline. The actual current efficiency would probably go as indicated by the dotted line.

The phases throughout dissolve almost quantitatively, with the exception of the γ phase which dissolves copper-rich.

TABLE 3

Corrosion in 7 percent sodium nitrate solution

Percent of copper in test piece	Corrosion in gram	Coulometer cathode gain in gram	Percentage current efficiency	Copper corroded in gram	Percent of copper corroded
4.5	0.0996	0.3336	94.03	0.0072	7.22
10.0	0.0759	0.3336	64.0	0.0123	16.21
15.1	0.0653	0.3336	49.3	0.0129	19.75
25.0	0.0591	0.3336	38.18	0.0141	23.86
35.2	0.0640	0.3336	35.66	0.0217	33.91
45.6	0.0805	0.3562	36.99	0.0242	30.06
50.5	0.0941	0.3562	40.83	0.0476	50.58
55.0	0.0822	0.3023	40.05	0.0460	55.90
72.3	0.1253	0.3733	41.80	0.0908	72.46
74.3	0.1367	0.3733	44.82	0.0979	71.61
74.8	0.1220	0.3068	50.00	0.0831	68.10
76.0	0.0876	0.3253	32.48	0.0642	73.29
77.0	0.0697	0.2936	28.40	0.0519	74.40
78.9	0.1002	0.2661	44.24	0.0652	65.00
80.0	0.0733	0.2213	38.63	0.0572	78.00
83.6	0.1881	0.3733	57.06	0.1573	83.60
84.2	0.2180	0.2985	82.43	0.1838	84.30
85.8	0.2298	0.3023	84.45	0.1964	89.90
86.4	0.2409	0.2985	89.38	0.2151	89.29
89.5	0.2741	0.3345	88.58	0.2458	89.67
90.0	0.2912	0.3480	89.82	0.2649	90.97
96.0	0.2498	0.3480	93.17	0.2440	97.60

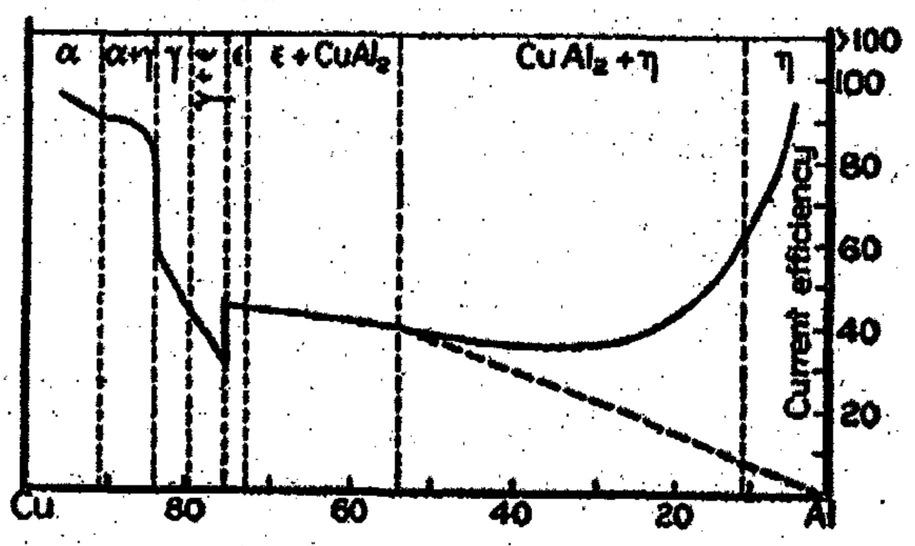

Fig. 4—Sodium nitrate solution

Electrolytic Corrosion in Sodium Chloride Solution

In Table 4 are given the results obtained from corrosion in a 7 percent solution of sodium chloride.

TABLE 4

Corrosion in 7 percent sodium chloride

Percentage of copper in test piece	Corrosion in gram	Coulometer cathode gain in gram	Percent current efficiency	Copper corroded in gram	Percent copper corroded
4.5	0.1000	0.3808	72.5	0	0
10.0	0.0943	0.3808	54.3	0	0
15.1	0.0316	0.3808	15.4	0	0
26.0	0.0265	0.3808	9.6	0	0
35.2	0.0579	0.3808	24.1	0	0
45.6	0.0511	0.2734	17.7	trace	—
50.5	0.0337	0.2734	6.4	trace	—
51.9	0.0207	0.2734	10.9	trace	—
58.8	0.0555	0.2734	15.6	trace	—
74.8	0.1222	0.3068	25.4	0.0323	26.4
78.9	0.1084	0.2661	24.8	0.0345	31.8
80.0	0.1049	0.2213	28.5	0.0400	38.1
82.0	0.1257	0.2768	26.8	0.0442	35.1
83.6	0.1607	0.3194	29.2	0.0766	47.7
86.4	0.2124	0.3665	32.7	0.1291	60.78
87.4	0.2648	0.3665	40.4	0.1895	71.56
89.5	0.4422	0.3665	66.2	0.3885	87.85
90.0	0.4544	0.3487	71.1	0.4126	90.8
96.0	0.5623	0.3487	83.4	0.5345	95.1

As shown in Fig. 5, the α phase dissolves with the highest efficiency. Its solubility decreases with the decrease in the copper content of the bronze. The γ phase is relatively insoluble and from pure α to pure γ in the $\alpha + \gamma$ field the efficiency drops from 70 percent to about 28 percent. Throughout the γ, the $\gamma + \epsilon$ and ϵ fields the efficiency drops off slightly and continues to fall through the $\epsilon + CuAl_2$ field. From here on and even in the $\epsilon + CuAl_2$ fields the efficiency is problematical, for the solutions going alkaline had a chemical effect upon the $CuAl_2$ and η phases. A dotted line represents what is probably the actual current efficiency.

The α phase dissolves practically quantitatively, but the γ and ϵ phases dissolve copper-rich and the copper in the $CuAl_2$ and η phases does not dissolve at all.

From 0 percent copper to where the ε phase exists pure, the corroded pieces were left at the end of the run with the copper very finely divided, on account of the aluminum having been dissolved out. On standing a short time the copper was oxidized in the air. The copper oxide then powdered and was inclined to fall off of the test piece. In each case the test piece and the oxide were reduced in order to obtain the exact weight of the test piece as it was immediately after the corrosion.

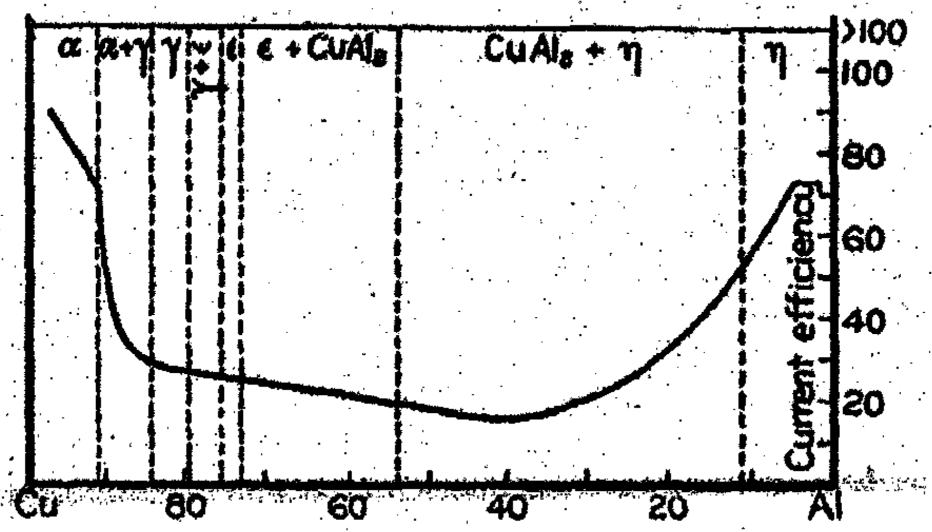

Fig. 5—Sodium chloride solution

It is interesting to note the following losses in weight of certain test pieces which had been allowed to stand three days until the copper was completely oxidized. At the end of that time the oxides were scraped off, leaving the test piece clean. In some cases a very considerable portion of the test piece had been corroded.

Percent of copper in test piece	Actual loss in gram	Loss with copper cleaned off
35.1	0.0579	0.1133
45.5	0.0511	1.5433
50.5	0.0337	1.0895
51.9	0.0207	1.0601
58.8	0.0555	0.8231

The actual loss was obtained from weighings made immediately after the test pieces were removed from the corroding solutions.

The efficiencies given for the sodium chloride solution are based upon the copper dissolving as cuprous chloride.

Electrolytic Corrosion in Sodium Carbonate Solution

Starting at 100 percent aluminum the efficiency of the corrosion of the aluminum bronzes in a 7 percent sodium carbonate solution is practically zero until the ϵ phase is reached. The solutions do not go alkaline at any stage of the corrosion and there is consequently no chemical action by NaOH. The efficiency as shown by Table 5 remains constant at about 10 percent, through the $\gamma + \epsilon$ phase. The α phase is somewhat more soluble, the maximum efficiency being 20 percent at pure γ.

The $CuAl_2$ and η phases become aluic and it was impossible to pass any current through the test pieces having composition in the $CuAl_2 + \eta$ and the η fields.

TABLE 5

Corrosion in 7 percent sodium carbonate solution

Percent of copper in test piece	Total corrosion in grams	Coulometer cathode gain in gram	Percent of current efficiency	Copper corroded in gram	Percent of copper corroded
4.5	0.0019	0.0172[1]	—	0	—
10.0	0.0035	0.0172[1]	—	0	—
15.1	0.0006	0.0172[1]	—	trace	—
25.0	0.0045	0.0172[1]	—	0.0018	—
35.2	0.0011	0.2350	—	0.0015	—
45.6	0.0045	0.0172[1]	—	0.0032	—
50.5	0.0054	0.2930	—	0.0043	—
58.8	0.0065	0.2930	—	0.0052	—
72.0	0.0108	0.2930	4.60	0.0055	—
73.0	0.0121	0.2084	7.19	0.0079	65.29
75.3	0.0206	0.2985	8.55	0.0149	72.32
84.2	0.0272	0.3162	9.71	0.0167	81.07
84.5	0.0243	0.2985	9.16	0.0197	61.40
86.4	0.0277	0.2350	13.04	0.0275	99.28
85.6	0.0485	0.3192	16.49	0.0371	76.50
90.1	0.0515	0.3192	17.33	0.0485	94.06

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[1] Impossible to get more current through, using entire battery voltage of 28 volts.

There was no hydroxide precipitated in any of the runs, the copper dissolving as sodium copper carbonate, giving a clear blue color to the solution.

The efficiency curve was not of enough importance to be shown.

Electrolytic Corrosion in Sodium Acetate Solution

From Table 6, showing the results obtained by the corrosion of the aluminum bronzes in a 7 percent solution of sodium acetate, and from the efficiency curve, Fig. 6, it can be seen that the ε, $CuAl_2$ and η phases are practically insoluble, the efficiency running between zero and 7 percent by experiment. With the introduction of the γ phase, however, it rises to about 12 percent or 13 percent increases to 19 percent with nearly pure α. With the increase in the copper in the α phase, the efficiency continues to rise, reaching about 50 percent with the 96 percent bronze.

TABLE 6

7 percent sodium acetate solution

Percent copper in test piece	Total corrosion in gram	Coulometer cathode gain in gram	Percent current efficiency	Copper corroded grams	Percent copper corroded
4.5	0.0014	0.1684	2.6	0	0
10.0	0.0047	0.2930	4.5	0	0
15.1	0.1508	0.3426	11.1	0.0187	12.4
35.2	0.0038	0.2930	2.4	0.0027	—
45.6	0.0024	0.2975	1.3	0.0010	—
50.5	0.0084	0.1684	7.7	0.0050	—
58.8	0.0055	0.2975	2.6	0.0093	—
65.4	0.0145	0.3426	3.8	0.0016	—
72.0	0.0035	0.3162	1.4	0.0000	0
73.0	0.0100	0.2084	4.0	0.0014	—
77.2	0.0196	0.3162	7.9	0.0012	—
78.9	0.0098	0.2936	3.9	0.0048	—
80.0	0.0075	0.2936	3.0	0.0048	—
82.0	0.0089	0.2768	3.6	0.0065	—
85.8	0.0321	0.3023	11.8	0.0291	90.0
87.4	0.0327	0.2602	13.9	0.0288	88.1
89.5	0.0346	0.2602	14.35	0.0256	74.0
90.1	0.0442	0.2602	18.25	0.0377	85.3
96.0	0.1181	0.2350	51.67	0.1056	89.4

As in the carbonate solution, the test pieces with a high percent of aluminum had a tendency to become aluic and no current could be passed through some of them. Where the efficiency runs very low, the total amounts corroded are too small to make the figures much more than indicative of the fact that there is a general tendency in all but the α phase not to dissolve in the acetate solution.

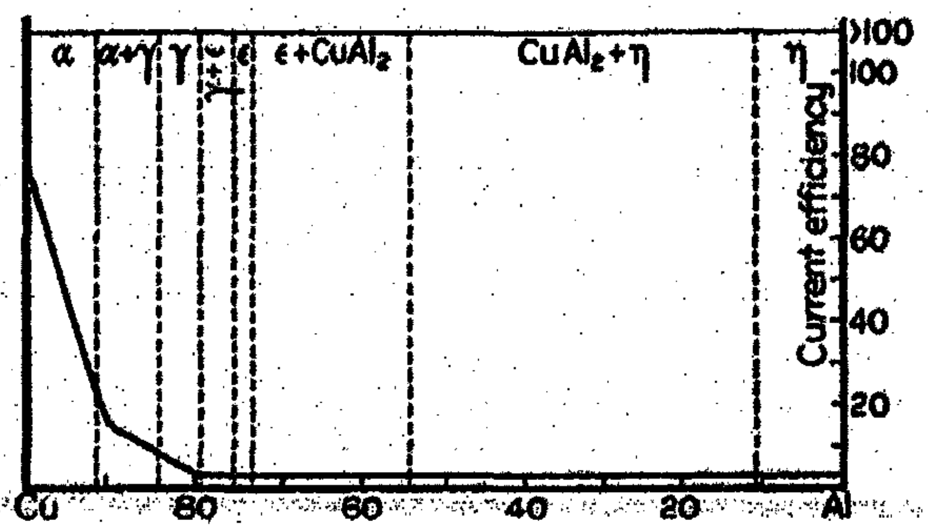

Fig 6—Sodium acetate

The solutions in all but the 96 percent test piece and those which became aluic early in the run, were all colored blue by the presence of the copper acetate. There was a slight hydroxide precipitate with the 96 percent copper piece.

The high result for the 15.1 percent piece is unaccounted for.

Electrolytic Corrosion in Acid Ammonium Oxalate Solution

Fig. 7 represents the efficiency curve of the solution of the aluminum bronzes in a solution of 7 percent ammonium

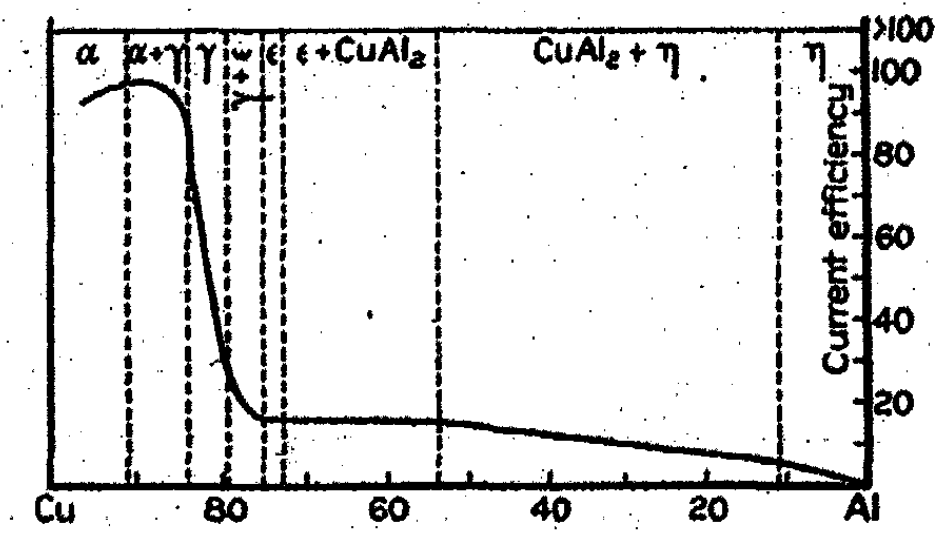

Fig. 7—Acid oxalate solution

oxalate and 3 percent oxalic acid, which was obtained from data in the following table.

TABLE 7

Corrosion in 7 percent sodium oxalate and 3 percent oxalic acid

Percent copper in test piece	Corrosion in gram	Coulometer cathode gain in gram	Percent of current efficiency	Gram of copper corroded	Percent of copper corroded
11.0	0.0054	0.2213	6.7	0.0013	—
15.1	0.0115	0.2638	11.2	T_2	—
35.2	0.0310	0.3151	18.29	0.0053	—
45.6	0.0234	0.1648	23.24	0.0026	—
58.8	0.0394	0.3154	17.7	0.0077	19.5
65.4	0.0455	0.3154	19.1	0.0261	57.4
71.8	0.0306	0.2795	13.7	0.0119	38.9
73.0	0.0479	0.3154	19.4	0.0216	45.1
76.0	0.0371	0.2638	17.0	0.0246	66.3
77.0	0.0422	0.2936	17.2	0.0278	65.9
78.9	0.0651	0.2661	28.8	0.0444	68.2
80.0	0.0486	0.2213	25.6	0.0338	73.7
83.6	0.1906	0.2792	77.3	0.1542	80.9
84.2	0.2576	0.3154	90.1	0.2022	78.5
86.4	0.2454	0.2792	97.3	0.2069	84.3
87.4	0.2457	0.2792	96.9	0.2041	83.1
89.5	0.2526	0.2792	97.7	0.2155	85.3
90.1	0.2833	0.3147	98.1	0.2464	87.0
96.0	0.2762	0.3147	90.7	0.2558	92.6

The α crystals dissolve more easily than the others and with a composition of 91 percent have an efficiency of 98 percent. With an increase in the copper content, the α crystals are slightly less soluble.

With the introduction of the γ phase the efficiency falls off until pure γ of 84 percent copper composition is reached and across the γ field it continues to decrease with the decrease in the copper content. Across the $\alpha + \gamma$ and the γ fields the bronzes corrode copper-rich to a slight extent. Compared with the α and γ phases, the ε phase is considerably less soluble, with a resulting drop in the efficiency across the $\gamma + \varepsilon$ field. In the ε and $\varepsilon + CuAl_2$ fields the efficiency is about constant, although the points across this field are not very well in line with the curve as drawn. The ϵ phase dissolves copper-rich, while in the ϵ + $CuAl_2$ field the copper goes into solution almost entirely from the ϵ phase as evidenced by the fact that no copper to speak of dissolves from the $CuAl_2$ + η field.

It was found very difficult to get any current through the test pieces containing the higher percents of aluminum, as there was a general tendency to become aluic. These pieces seemed to have a slight oxide film on them at the end of the run.

The total corrosion below the ϵ + γ field is so slight that the percentage of efficiency and the percent of copper corroded vary considerably. Experimental difficulties, coupled with the extreme brittleness of the ϵ and $CuAl_2$ phases make work in these fields rather open to error. At the same time the results are indicative of the general solubility of these bronzes.

There were some high efficiency values obtained for the 5, 10, 15 and 25 percent pieces but they have been omitted.

Electrolytic Corrosion in an Alkaline Tartrate Solution

The results obtained from the corrosion in the alkaline tartrate solution, 7 percent sodium tartrate and 3 percent of sodium hydroxide, are interesting. They were at first rather difficult to interpret but were finally made clear by use of the data obtained from the corrosion in sodium hydroxide, a few runs in a neutral tartrate solution and a large number of runs in the alkaline tartrate itself. The data in Table 8 and the efficiency curve in Fig. 8 show a gradual increase in the

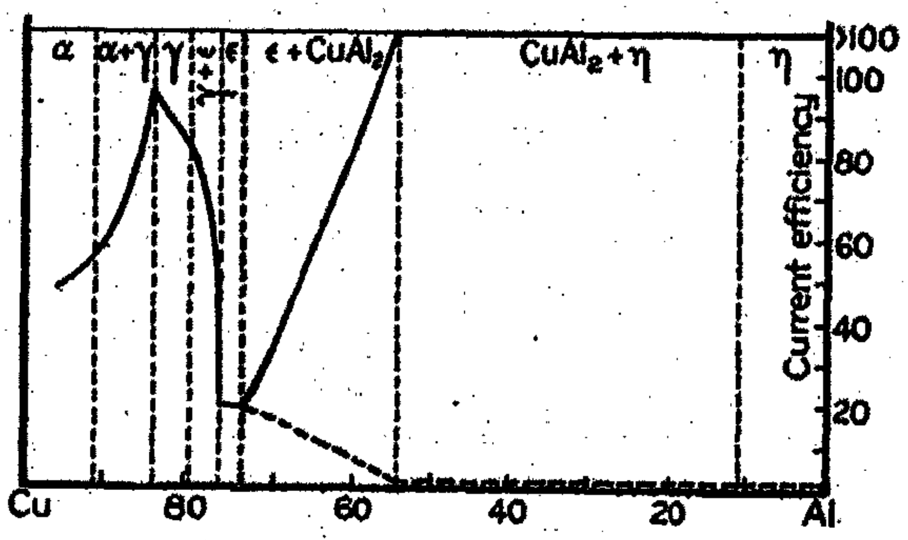

Fig. 8—Alkaline tartrate solution

efficiency through the α- and $\alpha + \gamma$ fields, reaching a maximum at pure γ. With the introduction of the ε phase, the efficiency drops off very rapidly and goes down to a bit less than 20 percent with the disappearance of the γ phase.

TABLE 8

7 percent sodium tartrate, 3 percent NaOH solution

Percent of copper in test piece	Corrosion in grams	Coulometer cathode gain in gram	Percent of current efficiency	Copper corroded in gram	Percent of copper corroded
0.0	0.3588	0.2147	> 100	0	0
4.5	1.6828	0.2147	> 100	0.0530	3.15
10.0	1.8280	0.2147	> 100	0.1511	8.30
15.1	1.3492	0.2147	> 100	0.1642	12.17
25.0	1.4226	0.2147	> 100	0.3457	24.30
35.2	1 1507	0.2147	> 100	0.3901	33.90
50.5	1.3668	0.2148	> 100	0.6120	44.77
51.9	1.4707	0.2147	> 100	0.6490	44.13
55.0	0.5314	0.3253	> 100	0	0
60.0	0.1811	0.3078	82.28	0	0
63.0	0.0883	0.2638	45.48	0	0
74.0	0.0480	0.3078	19.13	trace	—
76.0	0.0958	0.2638	43.81	0.0571	59.5
76.9	0.1731	0.3078	67.27	0.1284	74.1
80.0	0.2228	0.3078	84.42	0.1687	75.8
82.0	0.2086	0.2768	85.34	0.1543	73.90
84.5	0.2508	0.2795	95.47	0.1872	74.62
85.8	0.2283	0.3023	83.91	0.1815	79.50
86.4	0.2011	0.2350	94.96	0.1671	82.92
87.4	0.2916	0.5270	60.93	0.2230	76.47
89.5	0.2928	0.5270	60.00	0.2029	69.30
89.5	0.2887	0.5270	59.16	0.2085	72.22
90.1	0.2793	0.5270	56.91	0.2281	81.67
96.0	0.2483	0.5270	48.47	0.2444	98.45

By reference to Table 1, in the corrosion by sodium hydroxide, it will be seen that there is practically no corrosion of the α, γ or ε phases in that solution, and that the corrosion reaches a maximum at about pure $CuAl_2$. Therefore the total corrosion in the fields above 73 percent copper is due to the tartrate and not to the sodium hydroxide. Below 73 percent copper, however, as shown by Table 1 the solution of the aluminum out of the $CuAl_2$ phase takes place in the $\epsilon + CuAl_2$ field, and both copper and aluminum are dissolved from the $CuAl_2 + \eta$ and η fields. This causes the efficiency as actually determined in the alkaline tartrate solution to rise to over 100 percent at 54 percent copper. The greater part of the solution taking place below 73 percent is also due to the action of the sodium hydroxide upon the $CuAl_2$ and this, of course, increases with the increase of that phase through the $\epsilon + CuAl_2$ field.

The percentage of copper to the total weight corroded below 73 percent and above 54 percent copper, is very small, and therefore the majority of the corrosion in these fields is the solution of the aluminum alone. As seen by the table there was only a trace of copper dissolved in the field of pure ϵ. Again comparing with the sodium hydroxide corrosions, it is worthy of note that the tartrate is able to dissolve the aluminum out of the ϵ phase but that the sodium hydroxide has no effect upon it. The copper of the ϵ phase seems to be oxidized to cuprous oxide. In each case this was scraped off and taken as copper corroded.

From 54 percent to 0 percent copper the efficiency in the alkaline tartrate solution continues with over 100 percent efficiency. This is due entirely to the sodium hydroxide. To prove this, runs were made with test pieces containing 49 percent, 35 percent and 11 percent copper and in each case there was no corrosion though the test piece did not become aluic, the coulometer cathode gain being 0.3154 gram.

The dotted line from 73 percent copper (20 percent efficiency) is what would be obtained were it not for the chemical action of the sodium hydroxide. This was determined from the efficiency of the 73 percent test piece and from the fact that the pure $CuAl_2$ and η phases have been shown to be insoluble in the neutral tartrate solution.

Attention is called to the fact that the curve as actually determined has a gradual increase from 73 percent to 54 percent copper which is due altogether to the chemical action of the sodium hydroxide upon the $CuAl_2$ phase.

The α phase dissolves aluminum-rich and the γ phase almost according to its composition, the solution after corrosion being a little low in copper. The ε phase dissolves with no loss of copper.

Electrolytic Corrosion of Bronzes Annealed at 610°

Corrosions were made with the following test pieces: 83.6, 84.1, 86.4, 87.4, 98.5, 90.1 percent of copper in the chloride, sulphate and nitrate solutions. It was originally intended to run corrosions of test pieces containing copper down to 73 percent, so as to include the $\gamma + \Delta$ field but the test pieces with lower than 84 percent copper almost invariably broke on quenching.

No current efficiency curves have been given in these corrosions but a brief summary of the results follows.

TABLE 9

7 percent sodium chloride solution

Percentage of copper in test piece	Corrosion in gram	Coulometer cathode gain in gram	Percent of current efficiency	Copper corroded in gram	Percent of copper corroded
83.6	0.0639	0.1525	24.0	0.0082	12.8
84.2	0.0471	0.1525	17.7	0.0282	59.9
86.4	0.1542	0.1525	57.1	0.1358	88.1
87.4	0.1730	0.1525	63.0	0.1397	80.8
89.5	0.1954	0.1525	70.8	0.1757	89.9
90.1	0.2014	0.1525	72.0	0.1700	84.4

As seen in Table 9, in the sodium chloride solution the efficiency gradually decreases through the $\alpha + \beta$ and $\beta + \gamma$ fields from 72 percent to 17 percent at nearly pure γ, where the efficiency is similar to the efficiency of the pieces annealed at 500°. The β phase is nearly as soluble as the α and much more so than the γ phase. The α and β phases dissolve practically quantitatively, but the γ phase dissolves copper-rich.

TABLE 10

7 percent sodium sulphate solution

Percentage of copper in test piece	Corrosion in gram	Coulometer cathode gain in gram	Percent of current efficiency	Copper corroded in gram	Percent of copper corroded
83.6	0.0570	0.0743	86.9	0.0504	84.4
84.4	0.0565	0.0743	85.8	0.0428	75.8
86.4	0.0586	0.0743	87.3	0.0508	86.7
87.4	0.0583	0.0743	86.5	0.0511	88.0
89.6	0.0685	0.0743	99.6	0.0572	83.5
90.1	0.0725	0.0743	104.0	0.0633	87.3

In the sulphate solution the corrosion in the $\alpha + \beta$ field takes place with a higher efficiency than that of the $\beta + \gamma$ field, the first with 100 percent efficiency and the second at about 87 percent. The value of 104 percent for the 90.1 percent test piece is probably due to the mechanical dislodgement of either α or β crystals. By comparison with the sulphate solution (Table 2) it will be seen that there the α phase dissolves with slightly over 100 percent efficiency.

TABLE 11

7 percent sodium nitrate solution

Percentage of copper in test piece	Corrosion in gram	Coulometer cathode gain in gram	Percent of current efficiency	Copper corroded in gram	Percent of copper corroded
83.6	0.1267	0.1684	85.1	0.1028	81.2
84.2	0.1817	0.2619	78.5	0.1535	84.5
86.4	0.1809	0.2619	76.5	0.1552	85.8
87.4	0.1820	0.2619	76.5	0.1579	86.8
89.6	0.1941	0.2619	80.0	0.1664	85.7

In the nitrate solution the current efficiency through the $\alpha + \beta$ and $\beta + \gamma$ fields is about constant, the β phase being slightly less soluble than the α phase, while the γ phase is the most soluble of the three.

The fields here are rather narrow and yet the relative solubility of the α, β and γ phases is brought out fairly well. All of these phases in the three solutions used dissolve according to their composition with the exception of the γ phase in the sodium chloride solution, which dissolves copper-rich.

Summary

The corroding effects of the more common sodium salts and of sodium hydroxide upon the aluminum bronzes have been determined.

The organic acid salts, with the exception of the tartrate dissolve the α phase most easily. In the tartrate the γ phase is considerably more soluble. The $CuAl_2$ and η phases are practically insoluble in the organic acid salts used.

In the tartrate and sulphate the α is the most soluble, followed by the ε and γ while in the chloride the γ is slightly more soluble than the ε.

The α, γ and ε phases are practically insoluble in NaOH but the $CuAl_2$ and η phases are very readily soluble.

The bronzes practically do not corrode in the carbonate solution.

Unless caused by some additional chemical action, the changes in the rates of corrosion only occur upon the appearance or disappearance of a phase as shown in the equilibrium diagram.

There is a general tendency, except in the chloride and nitrate, and especially in the organic acid salt solutions for the bronzes high in aluminum to become aluic. This is accompanied by the formation of a thin film of aluminum oxide.

Unfortunately, the phases which have the greater resistance to corrosion are those which have the poorer physical properties. Were it not for the alkalinity of the solution as previously mentioned the efficiency curves in the $CuAl_2 + \eta$ and the η-fields would run very low. If that be true the alloy containing from 10 to 20 percent copper should be very serviceable for metal parts which are subject to the weather.

The expenses of this work have been covered by a grant to Prof. Bancroft from the Carnegie Institution, of Washington. The work has been done under the direction of Prof. Bancroft to whom the author is very much indebted for his advice and kind criticism without which the interpretation results could not have been made. Thanks are also due B. E. Curry for advice during the course of the work.

Cornell University.

NEW BOOKS

Solubilities of Inorganic and Organic Substances. *A Handbook of the Most Reliable Quantitative Solubility Determinations. Recalculated and Compiled by Atherton Seidell. 15 × 24 cm; pp. 367. New York: D. Van Nostrand Company, 1907. Price: $3.00 net.*—The author has given solubilities of inorganic substances in water, in organic solvents, and in mixed solvents. To a lesser extent this has been done also for organic solids. In addition, there are many data on distribution between two solvents. This in itself is good but the author has gone one step farther. He has recalculated the data so as to give the solubilities at regular intervals and he has also used his judgment as to what are the most reliable determinations. This last is a dangerous thing to do, but it is a thing which must be done if we are not to be swamped with superfluous and inaccurate data. The author is to be congratulated on his labor of love, and the book will be of great assistance to many people.

Wilder D. Bancroft

Thermodynamics. *An Introductory Treatise Dealing Mainly with first Principles and their Direct Applications. By G. H. Bryan. (B. G. Teubner's Sammlung von Lehrbüchern auf dem Gebiete der mathematischen Wissenschaften mit Einschluss ihrer Anwendungen. Band XXI). 16×23 cm.; pp. x + 204. Leipzig: B. G. Teubner, 1907. Price: bound, 7 marks.*—This is a carefully considered study of the principles of thermodynamics, by a man who is more than usually free from the common inability to see the wood for the trees. That the main framework of thermodynamic theory is the primary concern of the book is plainly indicated by its sub-title, An Introductory Treatise Dealing Mainly with First Principles and their Direct Applications.

Bryan makes the point, often felt by students of the subject, that the general consequences of the principles of thermodynamics should be presented separately from particular consequences that rest in part on independent hypotheses deduced from experiment; that confusion is certain to arise if this separation is not made. The distinguishing feature of Bryan's treatment of the general theory is his deduction of the ordinary forms of the fundamental laws of thermodynamics from the principles of the conservation and degradation of energy.

The material considered is arranged in three parts. The first part gives a general sketch of the more important facts and definitions of thermodynamics, as based on experience; and an account of such relations between thermal coefficients as are deducible independently of thermodynamic laws. The second part develops the general theory of the subject. The concluding part consists, in the main, of applications to radiation, to systems whose states are determined by two independent variables, to perfect gases, to systems having more than one independent component, and to thermoelectric phenomena; with a closing chapter on geometric and dynamic representations in thermodynamics.

The book affords an interesting treatment of thermodynamic theory, in small compass. It is a credit to the admirable Teubner series in which it appears.

J. E. Trevor

Sechs Vorträge über das thermodynamische Potential *und seine Anwendungen auf chemische und physikalische Gleichgewichtsprobleme. Eingeleitet durch zwei Vorträge über nichtverdünnte Lösungen und über den osmotischen Druck. By J. J. van Laar. 15×23 cm; pp. viii + 119. Braunschweig: Friedrich Vieweg und Sohn, 1906. Price: paper 3.50, linen 4.20 marks.*—The aim of these semi-popular lectures is to show the effectiveness of the theory of the thermodyamic potential in the treatment of various problems of chemical equilibrium. The lectures are really popular in tone, although their method is a mathematical one. Still, the mathematics employed involves nothing beyond elementary calculus.

In the two introductory lectures, the essential insufficiency of the theory of dilute solutions is emphasized, and the chief features of the theory of osmotic pressure are made clear. In particular, an osmotic pressure is considered as the pressure equivalent of a process of diffusion, it is shown that in an isolated solution this pressure is non-existent, and it is contended that for theoretical purposes the osmotic pressure is a secondary concept in comparison with the more fundamental one of the thermodynamic potential.

In the first three of the six lectures on the thermodynamic potential, various important qualitative relations of the phase theory are simply and directly obtained. The remaining lectures deduce, with a like simplicity, a variety of quantitative results concerning the dissociation of gases, evaporation, fusion, solubility, etc., and extend the treatment to the consideration of various electro-chemical equilibria.

The little book is written by an enthusiast, and it is interesting, suggestive, and clear.

J. E. Trevor

The Scientific Papers *of J. Willard Gibbs. In two Volumes. Vol. I: Thermodynamics. 16×26 cm; pp. xxviii + 434. Price: $5.00 net. Vol. II.: Dynamics, Vector Analysis and Multiple Algebra, Electromagnetic Theory of Light, etc. 16x26 cm; pp. viii + 284. Price: $4.00 net. New York: Longmans, Green and Co.*—It is indeed a matter for congratulation that the writings of Gibbs, especially those on thermodynamics, are now available in these handsome volumes. The first volume is occupied by the papers on thermodynamics. These comprise the introductory paper of 1873 on graphical methods, the beautiful paper on the energy surface of a one-component fluid, the great memoir on the equilibrium of heterogeneous substances, Gibbs's own abstract of this prepared for the *American Journal of Science*, the later computations of the dissociation equilibria of several vapors, two minor journal articles, the famous letters to the Electrolysis Committee of the British Association, and some unpublished fragments. The fragments relate to the preparation of a reprint of the author's thermodynamic papers, and are of considerable interest. Gibbs's papers on vector analysis and multiple algebra, and on other topics of mathematical physics, are assembled in the second volume.

The accessibility of this edition will do much to extend knowledge of what the present state of thermodynamics really is. Without a first-hand study of the work of Gibbs, such knowledge at present is simply unattainable.

J. E. Trevor

THE ELECTROCHEMISTRY OF LIGHT. I

BY WILDER D. BANCROFT

I. INTRODUCTION

J. M. Eder[1] says that most of the observations on the chemical action of the solar spectrum may be summed up as follows:

(1) Light of every color, from the extreme violet to the extreme red, and also the invisible infra-red and ultra-violet rays, can cause chemical action.

(2) Those rays which act chemically on a substance must be absorbed by it; the chemical action of light is connected closely with the optical absorption.

(3) Each color of the spectrum can have an oxidizing or a reducing effect, depending on the nature of the light-sensitive substance.

(4) Although one cannot distinguish sharply an oxidizing action of red rays and a reducing action of violet rays, one can say that, in general, red light has an oxidizing action on metallic compounds while violet light usually has a reducing action. A case in which red light can act as a reducing agent on metallic compounds is especially noticeable in the photography of the spectrum using silver salts and developing the picture. Violet and blue light have the most effect on compounds of the metalloids, for instance on hydrogen and chlorine mixtures, on nitric acid, on sulphurous acid, on hydriodic acid, etc. (Hydrogen sulphide, however, is decomposed more rapidly by red light.) The action of light is partly a reducing one, depending on the nature of the substance in question. On organic compounds (especially the colorless ones) violet light usually has the strongest oxidizing action; dyes are oxidized most strongly by those rays which are absorbed. In all cases however the chemical action of colored light comes under the law that those rays

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[1] Handbuch der Photographie, 2nd Ed., 1, 180 (1892).

are the most effective which are markedly absorbed by the light-sensitive substances.

(5) In addition to the absorption of light rays by the illuminated compound itself, the absorption by added substances is of importance in the chemical action of light. The light-sensitiveness of the first substance is often increased for the rays absorbed by the other substances (dyes as sensitizers).

(6) If we add to the light-sensitive compound a substance which reacts chemically with the radical set free by the light (oxygen, iodine, bromine, etc.), it increases the decomposition by light through predisposing affinity. Such substances are called chemical sensitizers.

(7) The action toward colored light varies much with the purity of the reacting compound, with its molecular state, and also with the method of developing the latent image in the case of silver salts (especially so with silver bromide).

(8) The direct decomposition of a compound (for instance, the blackening of AgI, AgBr and AgCl) by rays of light does not run parallel with the formation of the latent image and the development of the same.

(9) The activity of the solar spectrum varies markedly with the state of the atmosphere so that with the same elevation of the sun and an apparently clear sky the chemical effect is only rarely the same; absolute figures for the chemical action of differently refrangible rays of the spectrum cannot therefore be given with accuracy.

Some years later Ostwald[1] writes in the following way about the conversion of radiant energy into chemical energy. "While radiant energy can easily be obtained from heat and can be converted back as easily into heat, the transformations into chemical energy, though frequent enough necessitate special conditions in regard to its period and to the nature of the substance causing the change. Only rays of definite periods (often, however, comprised between fairly

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[1] Lehrbuch der allgemeinen Chemie, 2nd Ed., 1, II, 1024.

wide limits) cause chemical reactions in a given substance, and we must therefore conclude that a periodic supply of energy by means of radiation produces in substances periodic phenomena which cause an increased absorption of the energy supplied and consequently bring about corresponding chemical reactions. People usually picture these processes to themselves as due to elastic vibrations of molecules about a point of equilibrium and in this way establish a plausible parallel with the acoustic resonance phenomena. It must be remembered, however, that the goal of science is to obtain a conception of nature which shall be as free as possible of hypotheses and that to that end we should give up such pictures and should replace them by a determination of the conditions under which in general a rhythmical addition of energy produces a cumulative effect. It must be admitted that, in consequence of the mechanical hypotheses now prevailing, not even a perceptible approach to this goal has been made.

"In the following pages are collected the known facts in regard to the conversion of radiant energy into chemical energy. The name of photochemistry, which is usually applied to this field, is really too limited since the conversion is not limited to the visible rays; but it is not necessary to make a change because there is no danger of any errors."

Nernst[1] takes an even more pessimistic view of our knowledge of photochemistry and denies that an equilibrium can be displaced by light or that we can account in any way for the action of sensitizers like eosine or erythrosine. On the other hand, he was very close to what I believe to be the truth when he said[2] that it is quite possible "that in the chemical action of light we are dealing with phenomena analogous to the formation and decomposition of chemical compounds under the influence of the electric current."

In a previous paper[3] I have shown that the phase rule

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[1] Theoretische Chemie, 3rd Ed., 692–695.

[2] Ibid., 695.

[3] Jour. Phys. Chem., 10, 721 (1906).

applies to all cases of reversible photochemical equilibrium. This was very satisfactory as far as it went; but there are not very many cases of photochemical equilibrium and they are not the ones in which people are especially interested. The next problem was to bring the various catalytic actions of light under one head so far as possible. The object of this paper is to show that this may be done if we will avail ourselves of two laws put forward by Grotthuss some ninety years ago.

It seems probable that two of the laws of photochemistry are:

I. Only those rays of light which are absorbed can produce chemical action (Grotthuss).

II. The action of a ray of light is analogous to that of a voltaic cell (Grotthuss).

The first law is usually attributed to Draper;[1] but it was formulated by Grotthuss in 1818 in his paper on the chemical action of light and electricity.[2] As this law is universally recognized as true, it is not necessary to dwell upon it any further at present, though some of the evidence for it will be given later in this paper.

The second law of photochemistry was also formulated by Grotthuss in the same paper. The following extracts will bring out the point of view clearly.[3]

Section 3

"The usual methods of accounting for the chemical action of light do not seem to be successful in offering a clean-cut explanation which shall be in agreement with all the facts. At least, the otherwise clever ideas of Rumford, which I think are the ones most generally accepted by physicists, are not applicable here. Rumford believes that light heats

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[1] Phil. Mag. [3], 19, 195 (1841).

[2] Ostwald's Klassiker, 152, 94. Cf. Slater: Phil. Mag. [4], 5, 67 (1853); Draper Scientific Memoirs, 412 (1878). Goldberg: Zeit. wiss. Photographie, 4, 99 (1906).

[3] The section numbers are those of Grotthuss's paper published in the *Klassiker*.

certain elementary particles of a given substance to a very high temperature and thereby causes reactions similar to those produced at red heat, such as the decomposition of ferric chloride into chlorine and ferrous chloride.[1] If this view were right the red rays of the spectrum should have the greatest chemical effect because they have the greatest heating effect while the violet rays, which have only a slight heating power, should have only a slight chemical effect on substances which are changeable by light.

"In most cases, however, the exact opposite takes place, in proof of which I need only cite the case of horn silver, which is blackened much more strongly by violet rays than by red rays acting for the same length of time. The plausible and clever hypothesis of Rumford's is therefore no longer tenable.[2]

Section 4

"It is more general, and more in accordance with facts as I see them, to compare the chemical action of light with that of polar electricity (galvanism). Light separates the constituents of many ponderable compounds and forces them to form new compounds with its own imponderable elements (+E and —E), just as the poles of the voltaic battery do to a still greater extent. From this point of view it is easy to classify the chemical actions of light under simple and general heads, which are of importance in that they serve to enable us to predict what changes a compound will undergo in the light.

"The first general formulation may, I think, be expressed as follows:

I. From certain solutions, especially those which are easily decomposed without oxidation, deoxidation, chlorination or dechlorination taking place, light decomposes the salt in the solution into such parts that the new compounds resulting from this decomposition under the existing con-

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[1] Thénard: Traité de Chimie, 2, 573.

[2] Cf. Berthollet: Essai de Statique chimique, 1, 198.

ditions have the greatest possible difference of solubility in the solvent employed.

"As an instance of this I cite the solution of stannous chloride in water. If this solution is placed in two stand-glasses and covered with pure oil to prevent oxidation, my own observations show that the solution becomes much more turbid in the glass which has been exposed to the sun's rays for five or six hours than in the other glass which was kept in the dark for the same length of time. There is formed a white insoluble stannous sub-chloride while an acid stannous chloride is formed at the same time and remains in solution.

"In the same category I place the solution of iron cyanide in hydrocyanic or prussic acid from which, according to Porrett,[1] light precipitates a white substance, iron cyanide sub-hydrocyanide; at least at first, while a small amount of iron cyanide must remain in solution with a great deal of hydrocyanic acid.

"The solution of ferric chloride in alcohol also belongs in this category for light precipitates at first a ferric sub-chloride while an acid ferrous chloride (through reduction by alcohol) remains dissolved in the liquid. Only later is the precipitated ferric sub-chloride reduced at the expense of the alcohol or perhaps of the acid, and then dissolved by the acid solution forming an (acid) ferrous chloride.

Section 5

"A second general formulation of the chemical action of light is as follows:

II. In an oxygen or chlorine compound which is changed by light, the light usually deoxidizes or dechlorinates the ponderable, electropositive, usually solid, constituent or prevents its oxidation or chlorination; and at the same time oxidizes or chlorinates the electronegative (or also indifferent), usually liquid, or gaseous, or also its own imponderable (+E), constituent. But also out of this first ponderable compound, a continued action of light may also remove the more

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[1] Schweigger's Jour., 17, 263.

remote constituents according to the same law especially with the aid of water. The action will not cease until the light has brought about the most complete separation of the ponderable substances and has made new compounds of the same with its own imponderable elements (+E).

"Absolute oxidation, hydrogenization and chlorination can never occur any more than can absolute deoxidation, dehydrogenization and dechlorination. These could only take place if it were possible to prepare oxygen, chlorine (gaseous chlorine contains +E, and crystallized chlorine at least water chemically combined), each absolutely alone (isolated). Each deoxidation, dehydrogenization, or dechlorination caused by light is consequently always necessarily accompanied by a simultaneous oxidation, hydrogenization or chlorination either of a ponderable or an imponderable substance; these so often misused terms are really only relative and usually refer only to those changes which the ponderable matter has undergone.

Section 6

"These two general cases of the chemical action of light have never before to my knowledge been presented so simply and so clearly, although they without doubt summarize a large series of facts observed by many physicists. Probably this is due to the fact that hitherto people have not considered the numerous phenomena from the point of view of polar electricity though this leads us to the simplest and clearest conceptions. In the articles on this subject the chemical phenomena of light are usually grouped under two heads and the authors cite instances of oxidation and deoxidation by light, apparently without considering the matter from a broader standpoint and noticing that neither of these two changes can occur without the other taking place simultaneously.

"The application of these generalizations to the explanation of the coloring of horn silver (according to Scheele's careful and conclusive experiments[1] a true reduction); to the

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[1] Cf. Scheele's Physical Chemical Works, edited by Hermbstädt, 1, 136.

decolorizing of gold and iron tinctures to the blackening of stannous chloride dissolved in alcohol;[1] to the preparation of the oxides of gold, silver, mercury, lead and other metals; to the phenomena observed by John Davy of the non-chlorination of mercury and the chlorination of carbon monoxide gas where a mixture of the three substances are exposed to light; all this, I say, is so simple that I do not need to go into details......"

"A ray of light is therefore a line along which the elements of neutral electricity arrange themselves in a polar fashion. Since the polarity does not involve any actual measurable separation of the two electricities but only a tendency to the separation and to the alternating molecular recombination of the same, it of course can no more be detected with an electrometer, which only shows the separated ∓E, than it can when the elementary particles of water assume a similar polarity or tendency to mutual separation during the formation of a metallic tree...."

"According to my idea, one might compare each single ray of light to a linear voltaic cell without the introduction of a conductor of the second class; but one must not compare the solar spectrum as a whole with the voltaic cell. It is also easy to see that such a linear cell, as I imagine a ray of light to be, could not produce a movement of the electrometer or a muscular contraction; because in it the two electricities do not appear separated by means of ponderable substances, but only show a momentary tendency to separate from each other. It would be just as impossible for this linear cell (the ray) to produce chemical changes, were it not that the imponderable elements of each pair of plates (±E)[2] possess the remarkable property of themselves combining chemically with and of being chemically attracted by the compounds decomposable by light. To this circumstance is due the fact that the tendency to separate is increased until it becomes a real separation of the elements and gives

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[1] My own observations.

[2] Sit venia verbo.

rise to new compounds. To this chief cause of the chemical action of light is often to be added what is usually a favorable factor that the light finds water in the substances to be acted on and this water increases the action by taking the part of the conductor of the second class, which is missing in the linear cell......"

Section 19

"Earlier in the paper I mentioned the remarkable decolorization which the blood-red tincture (ferric sulphocyanate in alcohol) undergoes in sunlight. The ferric salt is changed into ferrous salt by light just as much as by a reducing agent, and either the acid or the alcohol is oxidized. This case belongs under formulation II as given in Section 5. The blue starch iodine solution is not only gradually decolorized by light (as I have already mentioned in Section 8) but also by standing over iron filings and through contact with many other reducing agents (even by a sufficient quantity of alcohol). If iodine is a simple substance, a hydrogenization of the iodine must take place, either through water being decomposed or through the hydrogen of the starch combining with the iodine to form hydriodic acid and this combining with the altered (dehydrogenized) starch to form iodide. That the decolorized solution contains hydriodic acid can be shown by testing with silver nitrate solution. A white precipitate is formed which does not dissolve perceptibly in caustic ammonia. If one adds carefully a few drops of liquid chlorine to the decolorized solution, the hydriodic acid is decomposed and the blue color reappears immediately. From this I conclude that there is no white starch iodine compound as has been assumed by Colin and Gaultier.[1] Furthermore, these chemists, and others, who have worked at this problem, seem to have overlooked the most important condition for producing the blue color. The presence of water is absolutely necessary; for dry iodine ground up with dry starch does not become blue until it has

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[1] Schweigger's Jour., 13, 453.

become wetted either by taking up water hygroscopically or by a direct addition of water to the brownish mass. If one pours a drop of the brown solution of iodine in alcohol on dry starch, there appears a brown or a brownish-yellow spot which however becomes blue instantaneously on addition of a drop of water. The blue compound seems therefore to be a starch iodine hydrate. Its decolorization in light can therefore, as before said, be ascribed to the hydrogenization of iodine. The following seems therefore to be a third general formulation of the chemical action of light.

III. Light acts on compounds, whose constituents have a tendency to take up or to lose hydrogen, in such a way that it hydrogenizes the electronegative constituent (the iodine in the case under consideration), and dehydrogenizes the electropositive or also the indifferent constituent; while at the same time the imponderable elements of the light (+E) unite chemically with the newly-formed compounds (namely the hydriodic acid and the altered starch in the case just cited).

"In passing I will also mention that, from the colorless solution of starch iodide in a flask half filled with air, a rusty slimy precipitate separated after several days. When this precipitate together with the supernatant solution was exposed to the light it became dark indigo-colored after a week and nearly black after still longer time. The precipitate is probably starch iodide containing iodine and the change to black when exposed to the light in a flask containing water and air points to an oxidation of the hydrogen of the hydriodic acid whereby gradually indigo-colored starch iodine is formed again. The color of the starch iodine solution is distinctly violet or purple and therefore the yellow and green rays of the spectrum cause the maximum chemical effect."

In experiments on the behavior of ferric sulphocyanate dissolved in alcohol, Grotthuss found that when air was kept away from the solution, sunlight caused the red color to disappear. If the solution was placed in an unstoppered flask and exposed to the light, it was decolorized in the morning, reddened at noon, and decolorized again in the afternoon. Grotthuss set himself to the task of accounting for this difference in the action of the sun's rays at different hours of the day.

Section 30

"In order not to involve the reader in the medley of ideas into which I fell while investigating the abstruse phenomenon, and in order to make the deciphering of the puzzle more easy I will cite at once one fundamental experiment which is very simple and entirely conclusive. It proves the following points:

(1) The coloring of the tincture at noon does not depend at all on the greater heat of the atmosphere at this time of day; but on a *specific* action of *light* which manifests itself in a very remarkable, previously unknown contrast between the chemical action during the noon hours and during the morning and evening hours.

(2) This contrast in the chemical action of the light is due to two causes, namely (*a*) that in the morning and evening hours the rays of light are nearly parallel to the surface of the liquid and therefore pass directly into the solution from a *non-oxidizing* medium, the glass walls of the flask in which the tincture is contained. On the other hand (*b*) the rays at the noon hours are more nearly perpendicular and pass into the solution from an *oxidizing* medium, the oxygen of the air.

"One of two identical, low, crystallizing flasks having thin glass walls was covered to the top and four-fifths of the way round with a thin but close black paper put on with bookbinder's paste. One-fifth of the circumference was purposely left uncovered so that one could look through it at the uncovered bottom of the flask and could detect any changes which might take place in the solution. After the paper was entirely dry both flasks were filled to one-fourth of their total height (which is not quite two inches) with a colorless tincture of ferrous sulphocyanate and were placed together in the sunshine at noon on a clear summer day in July. Both flasks stood side by side on the same stand before the window. The dish covered with black paper was turned paper side to the light so that the solution received no light but could be heated as result of the absorption of the rays in the black paper. In half an hour the tincture in the unprotected flask was distinctly red and by one o'clock in the afternoon was redder than raspberry juice. At two o'clock the flask covered with paper was completely colorless and it remained so throughout the day.

"This instructive experiment is not one of those which gives a doubtful result, as is often the case with experiments on the solar spectrum made by physicists. The action is not only to be recognized but is quite striking and never fails when the experiment is performed under the conditions described. I have repeated the experiment often and have changed the paper covering from one flask to the other, thinking that the form or material of the flask might have an effect. The result was always the same. The flask with the paper on was a little warmer than the other, as could be told by touching them; therefore the reddening should have been more marked in the first if it were due to a greater evaporation and not to a special reaction of the oxygen of the air with the solution under the influence of light. That a too rapid evaporation was not the reason for the solution in the coated flask not becoming red is shown by the following facts: (1) that both solutions had lost but little in volume after standing in the sun for two hours so that there was no perceptible difference between them in this respect, (2) that on the edge of the surface of the two solutions there was not the slightest sign either of a red or of a gray solid residue, (3) that in all these experiments a thermometer with a blackened bulb standing in the sun by the flasks never registered higher than 38° R. and often not so high (4) that a portion of the same tincture when heated to 38° R. (in an open flask like the others, in which the solution would not evaporate rapidly on account of the narrow neck) showed no signs of change even after three hours, a reddening taking place first at 48° R. and a precipitation of a grayish mass first at 60° R.

Section 31

"Not only at noon, but also in the morning and evening I have been able to detect a slight reddening in the colorless tincture when exposed to bright sunlight. The effect was only noticeable after three hours' exposure and then only on condition that there was but a thin layer of solution, a quarter of an inch thick, in the flask which was one and a half inches in diameter. If the layer of solution was much deeper in proportion to its diameter, as in the case of the narrow cylindrical stand-glasses described in Section 25, which were four or five diameters high, the reddening did not occur till after ten in the morning while the opposite effect, namely the decolorizing, takes place before ten and after four. This observation proves that the form of the solution is of importance, and that the reddening is greater the larger the amount of light coming from the air into the horizontal surface of the solution relatively to the amount of light coming from the side through the glass directly into the solution.

"There are many other experiments which I could cite in support of this; but I omit them because those already discussed are sufficient to explain these interesting phenomena. From the experiments cited we may deduce the following conclusions, especially for the case of the solution being in contact with the air.

(1) The clear ferrous sulphocyanate tincture is only reddened in sunlight when the rays make such an angle with the horizontal surface in contact with air that the rays pass *directly* from the air into the *solution.*

(2) The reddening reaches its maximum at the time the sun is highest in the heavens (at noon) and therefore stands in relation with the size of the angle of incidence, *i. e.*, with the sine of the angle, which is a measure of it.

(3) In any other direction in which the rays do not come simultaneously in contact with the air and the colorless

solution, this latter is not only not reddened; but on the contrary a reddened tincture is gradually bleached completely.

Section 32

"The reddening occurs only when light, air and colorless tincture are all three simultaneously in contact each with the other two. If the liquid in the flask has a form which is higher than it is broad, relatively little light during the morning and evening hours passes direct from the air into the tincture because most of the rays are nearly parallel with the surface of the solution. On the other hand the rays pass in relatively much greater numbers perpendicularly through the glass walls of the flask into the solution. From below the uppermost layer of the solution to the bottom of the flask, the solution may be considered as shut off from air because the uppermost layer prevents the air from diffusing down. Consequently, during the morning and evening hours practically only light and tincture react together and the result of that reaction is the decolorizing of the reddened tincture and not the reddening of the colorless tincture. If this view is right, it occurred to me that reddening must also occur not only when light passes from the air into the solution, but also when it passes directly from the solution into the air, because in this last case, light, air and tincture are all simultaneously in contact. The following experiments prove the accuracy of this view and complete the explanation deduced from the simplest assumptions.

Section 33

"I filled a large glass tube, five lines in diameter and six inches high, half full with the red tincture, and stood it upright, and, by means of a concave mirror, passed a concentrated beam of light into it, sometimes perpendicularly to the walls of the tube and sometimes at an angle, but always so that the light did not pass through the surface of the solution in either direction. I turned the tube from time to time so that it should not heat too much in any one place. The solution became gradually cloudy and in a few minutes the color had entirely disappeared. I now tipped the tube as far as could be done without the solution coming out, rotated it from time to time, and passed light into the solution by means of the concave mirror in such a way that the light passed into the liquid from the bottom of the test-tube and passed out of the liquid directly into the air. In about thirty minutes the tincture was distinctly colored. This coloring and decolorizing of one and the same solution can be caused merely by changing the direction of the rays and I could repeat this as often as I wished until the salt in the tincture was completely decomposed. The reddening was shown even more clearly when I poured the colorless tincture into an open glass dish so that there was a thin layer of solution with a large surface; and then passed the light into the solution from below, taking precautions to prevent over heating.

"I next filled a little flask with the colorless tincture in such a way that the surface of the liquid was only a couple of lines below the mouth of the flask, placed it in the shadow and passed the rays of light from a plane mirror to a convex mirror and from this directly down through the mouth of the flask. In less than twenty-five minutes the tincture in the neck of the flask became red and drops like blood sank down, coloring the entire solution."

"The phenomenon of the coloring and the decolorizing of the tincture by light is obviously a specific action of light which is quite independent of the heat produced. It is true however that both phenomena can be produced by dark heat without light being necessary, the time required being dependent on the degree of heat. If one wishes to reason from the identity of many of the known chemical actions of light and heat, to the identity of the nature of the two principles, I have no objections. If one actually assumes, as Rumford,[1] Berthollet,[2] Thénard and Gay-Lussac[3] are in-

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[1] Philosophical Papers, Vol. I.

[2] Essai de Statique chimique, 1, 202.

[3] Recherches physico-chimiques, 1, 206.

clined to do and have done, that the chemical phenomena of light are due only to the heat evolved by the light in so many substances, I bring forward the following arguments against this last assumption:

(1) There are cases in which the chemical action of light takes place more certainly, the less the rise of temperature in the substance acted on by the light. In my experiments with the red iron tincture I tried often to keep this as cool as possible by dipping the flask containing the tincture into a glass filled with ice-cold water. When I focused the light on the solution with the concave mirror, decolorization took place rapidly although the solution was not heated to the point to which it would have been raised by the noon-day sun on a hot summer day and no concave mirror. The decolorization took place however much more rapidly in the first case than in the second.

(2) Diffused daylight, which cannot raise the thermometer a single degree even when concentrated by a concave mirror, decolorizes the red tincture although very slowly, in the course of several weeks. According to Gay-Lussac and Thénard diffused daylight brings about the chemical combination of a gas mixture consisting of chlorine and hydrogen although a very transparent substance like a gas can scarcely be heated much even by the strongest light and although dark heat will not produce the same result at a lower temperature than 120° C.[1]

(3) Those rays which have the least heating power (the violet rays) often (and sometimes solely) cause greater chemical reactions than the red rays which have a greater heating power. The converse is also true.

(4) If one is to assume that light only produces chemical changes by means of the heat which it generates in the smallest particles of the compound (heat which is never produced to the extent predicted and which often is not noticeable), one has just as much right to assume that heat can produce

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[1] Gay-Lussac and Thénard: Recherches physico-chimiques, 1, 202.

these results only through the light which always accompanies the reaction even though it may not be visible to our eyes."

"The theory which I have expounded here and also four years earlier[1] groups both phenomena of nature, light and heat, and consequently all the chemical actions of these two, under a higher general principle, namely under electricity. This last is to be looked on as the fundamental cause of all chemical changes which are brought about by light and heat. Since light and heat are alike in their nature or substance and differ only in the way they appear, it follows that their chemical actions must be similar. A result of this view is that a substance becomes heated when neutral electricity piles up in it. A substance becomes colder when deprived of neutral electricity (*i. e.*, heat). Light is the polar tendency of the elements (±E) of neutral electricity to separate or to combine...."

Section 37

"According to Pfaff's observations a bleached Bestuscheff's nerve tincture and also a bleached solution of ferric chloride in sulphuric ether, when kept under a large glass globe in contact with air, will become colored yellow after several days' exposure to light.[2] Since direct sunlight always produces all the positive effects of colored light in an intensified degree, it is practically certain that this coloring would also take place in direct sunlight if the experiment were carried on under otherwise the same conditions. It is probable that, in Pfaff's experiments, the tincture was present as a thin liquid layer, for if these colored solutions are placed in narrow test-tubes, they are always decolorized by sunlight even when in contact with air, as in Pfaff's experiments. These tinctures therefore appear to behave like the red ferric sulphocyanate tincture where the ferrous salt was oxidized

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[1] Schweigger's Jour., 14.

[2] Ueber Newton's Farbentheorie, 175. The coloring does not take place in the dark.

by light only when the rays pass directly from the air into the solution. This leads me to set up a fourth general formulation, under which in the future other substances will certainly be classed:

IV. If light is in direct and simultaneous contact with oxygen gas and with certain salt solutions (or also with soluble salts) which have already undergone a change through light or through some ponderable substance producing the same reaction, the light deoxidizes the imponderable +E of the oxygen gas and oxidizes the proximate electropositive constituent of the salt. After oxidation, light will deoxidize the same constituent provided oxygen gas be kept carefully away from the points of contact between light and the solution...."

This theory of Grotthuss has not as yet received the recognition which it deserves. J. M. Eder[1] sums up the paper as follows:

"Grotthuss tried to bring the chemical action of light in line with galvanic action. He considered positive electricity (+E) and negative electricity (—E) as the true components of light and expressed the view that light separates the constituents of many compounds and forces them to combine with electricity.

"He endeavored to bring all the photochemical phenomena known at his time under four laws and in order to prove his theory he made numberless new experiments which have done much to increase our knowledge of the light-sensitiveness of chemical substances. The four laws of Grotthuss are:

(1) From certain solutions, especially those which are dissociated, light separates the proximate constituents in such a way that the new compound resulting from the separation shows the greatest difference of solubility under the given conditions. (Example: a solution of stannous chloride in water, covered with oil, decomposes more rapidly in sunlight than in the dark. Basic stannous chloride precipitates and the acid salt remains dissolved.)

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[1] Handbuch der Photographie, 2nd Ed., 1, 86 (1892).

(2) In oxygen or chlorine compounds which are decomposed by light, the light usually deoxidizes or dechlorinates the ponderable electropositive constituent or prevents its oxidation or chlorination; at the same time the electronegative or the neutral constituent is oxidized or chlorinated. (Example: the action of light on silver chloride first sets free chlorine and this reacts with water to form hydrochloric acid, the oxygen of the water combining with the (+E) of the light and silver with the (—E) of the light; decolorization of the iron tincture).

(3) In compounds, whose components may be hydrogenized or dehydrogenized, light acts in such a way that the electronegative constituent is hydrogenized while the electropositive constituent and its imponderable element (+E) separates chemically from the resulting new compound. (Example: aqueous starch iodide becomes colorless in sunlight, hydriodic acid being formed.[1])

(4) When light reacts with oxygen and certain salt solutions which have already been changed directly by light or in the same way by other means, the light deoxidizes the imponderable (+E) of the oxygen gas and oxidizes the proximate electropositive constituent of the salt, etc., etc. (Example: the blood-red solution of ferric sulphocyanate is decolorized by light alone, but reddened again by the joint action of light and air.)

"At that time electrochemical theories were especially in favor with famous chemists (Davy, Berzelius and others) and it is clear that these theses are a result of an attempt by Grotthuss to apply these electrochemical theories—without much luck—to photochemistry."

A more correct view of the paper is taken by Luther.[2] "Much that Grotthuss has written appears to us to-day as fantastic and unintelligible. For all that, his conception of heat and light as electrical phenomena and his conception of

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[1] This reaction was afterwards recognized as merely a driving out of iodine by heat and the illustration is therefore not pertinent.

[2] Ostwald's Klassiker, 152, 198.

photochemical processes as electrochemical ones are brilliant prophecies which are to some extent only now receiving their scientific confirmation and experimental foundation."

The paper of Grothuss is hard reading partly because the German style is very bad and partly because the chemistry of that time seems strange to us. In many cases however it would take but a slight change in the wording to make it quite modern. For instance, in the decomposition of silver chloride by light, Grotthuss says that the silver combines with the +E of the light. We say that in the electrolysis of a silver salt, the positively charged silver ion is converted into silver either by losing its positive electric charge or by having the positive electric charge neutralized by a negative charge. The only real difference between these two cases is that one way of speaking is familiar to us and that the other is not.

The important question, however, is not whether the four generalizations of Grotthuss are well chosen. It is whether the fundamental conception is sound, that the chemical action of light is essentially electrolytic in nature. At the time Grotthuss wrote his paper, electrochemistry was in its first stages and he had very few facts on which to draw. To-day the situation is quite different and it ought to be possible to decide in how far the theory of Grotthuss describes the facts. The object of this paper is to apply the theory of Grotthuss to the facts and to demonstrate the extraordinary value of the theory. Since there is an apparent distinction between the cases in which light forms or destroys compounds and those in which light merely produces allotropic changes, I shall treat these two sets of phenomena separately.

II. ACTION OF LIGHT ON SALTS

Practically all the salts of silver are decomposed by light under some circumstances, the final product being either silver or some other reduction product. The decomposition products are the same as those obtained by electrolysis. Ferric chloride, sulphate, oxalate, tartrate, citrate and sulphocyanate are decomposed by light under suitable circumstances with formation of the ferrous salt, just as would happen if the solution were electrolyzed. The double ferric oxalates and the ferricyanides are reduced by light and by electrolysis. In presence of a suitable oxidizing agent such as oxygen, ferrous sulphate or sulphocyanate is oxidized to the ferric salt. It is a matter of common knowledge that ferrous salts can be oxidized electrolytically. Cupric chloride or bromide can be reduced by light to the corresponding cuprous salt and electrolytic action produces the same result. Light precipitates cuprous oxide from Fehling's solution and cuprous oxide is precipitated at the cathode when the solution is electrolyzed. While cuprous chloride is said to be changed by light there seems to be some question as to the reaction products so that we need not consider this case. From mercuric chloride and mercuric oxalate, light and electricity both precipitate the mercurous salt. Mercurous chloride is decomposed by light into mercury and mercuric chloride which are the electrolytic decomposition products of mercurous chloride. Mercurous oxide behaves like mercurous chloride. The reverse reaction is said to take place in presence of oxygen. From the salts of gold and platinum it is easy to obtain the metal either by the action of light or electrolytically. There seems to be some question as to the extent to which lead salts are changed by light but the alleged changes are those which electrolytic action would produce.

Chromic acid and the bichromates are reduced by light in presence of glue or many other organic substances; light reduces uranyl salts to uranous salts when in contact with paper; permanganate, manganese peroxide, manganic oxide and manganous hydroxide are all light-sensitive under certain conditions, as are also molybdic acid and the alkali salts of vanadic acid. With these salts of chromium, uranium, manganese, vanadium and molybdenum, the decompositions produced by light are identical with those produced by electrolytic action.

In many of the cases cited, the salts are light-sensitive only under certain conditions and it is now necessary to consider what the fundamental conditions are which make it possible for light to decompose the salt of a metal. So far as we know, the electromotive force of light is low, probably rarely exceeding half a volt.[1] We must therefore start with a salt having a low decomposition voltage or else we must add something to the solution which will lower the decomposition voltage. In other words, we must add a depolarizer. This appears clearly from the work of Grotthuss though of course he does not speak of decomposition voltages or of depolarizers. Ferric chloride in water is practically non-sensitive to light. In alcoholic solution it is reduced by light to ferrous chloride. The reason for the difference is that chlorine reacts readily with alcohol but not readily with water. On the other hand Grotthuss found that ferric sulphate in alcohol was only acted on very slowly by light. The reason for this is that alcohol is not a good depolarizer for oxygen but is a good one for chlorine. Grotthuss added alcohol to a stannous chloride solution and found that metallic tin was precipitated when the solution was exposed to light. This reaction needs further study because it seems probable that the reaction takes place in two stages with the oxidation of alcohol to aldehyde by the oxygen of the air as the first stage. If so, this would be another instance of reduction by means of an oxidizing agent.[2]

The light-sensitiveness of all substance is increased by the presence of a suitable depolarizer, and, in many cases, we get light-sensitiveness only in presence of depolarizers. The following passage[3] shows that this has been recognized quite clearly for many years:

"Certain substances (such as silver oxide, silver chloride, mercuric oxide) are decomposed directly by light, whereas others are only acted upon in presence of a substance which

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[1] Moser: Eder's Handbuch der Photographie, 2nd Ed., 1, 188 (1892).

[2] Luther: Zeit. Elektrochemie, 8, 647 (1902).

[3] H. W. Vogel: Handbuch der Photographie, 4th Ed., 1, 73 (1890).

can combine with one of the decomposition products. In this second group belong ferric chloride, chromates, etc. These are decomposed by light in presence of organic substances (ether, paper, etc.) which absorb the constituent set free (oxygen or chlorine). Water is decomposed in presence of chlorine which combines with the hydrogen set free, forming hydrochloric acid. These foreign substances, which make possible the decomposition of many compounds by light, play an important part in photography even when one is dealing with a compound which is directly light-sensitive, because it is decomposed much more readily under these circumstances.

"People used often to ignore the important effects of these other substances which are frequently present even in so-called chemically pure substances and it therefore happened that there was a marked discrepancy between the observations of different investigators on the decomposition of many compounds by light. Thus, until very recently, people disputed whether silver chloride was reduced by light to a subchloride or to the metal. The author has proved that both statements are correct depending on whether one lets light act on *pure* silver chloride or on silver chloride spread on paper. The organic fibres of the paper act directly or indirectly to absorb chlorine. To this is due the important effect on photographic processes caused by the methods of preparation of paper, collodion, gelatine, etc. Important effects may even be due to traces of precipitating agents which usually adhere to precipitates.

"We can therefore divide the light-sensitive compounds of the metals into two classes; into the *directly light-sensitive*, which are decomposed by the action of light alone; and into the *indirectly light-sensitive*, which are only decomposed in presence of a substance which combines with one of the decomposition products."

An interesting case of a depolarizer is silver nitrate and silver iodide. The silver nitrate can react with an iodide and consequently makes silver iodide more sensitive to light. This is pointed out clearly by Vogel.[1]

"Silver bromide and silver iodide under a silver nitrate solution are colored darker and more rapidly by light than when in the pure state. With silver chloride this effect is less marked. Silver bromide is colored dark violet while silver iodide becomes a dark green. The author has shown that pulverulent metallic silver is formed when light acts on silver iodide under a silver nitrate solution.

"The intensified decomposition is shown by the author's experiments to be due to the powerful chemical absorption of free bromine and iodine by silver nitrate because other substances which react with iodine also increase very markedly the rate at which silver iodide is decomposed by light. Examples of this are tannin, pyrogallol, ferrocyanide of potash, morphine, sodium arsenite, potassium antimonyl tartrate. Silver iodide is scarcely sensitive to light at all when precipitated by an excess of potassium iodide, but it becomes sensitive when treated with any of the substances just mentioned. Under some circumstances, paper fibres also act as sensitizers. Paper impregnated with silver chloride or silver bromide is colored by light much darker than pure silver chloride or bromide, the former giving a deep chocolate brown color and the latter a violet color. Through the action of the organic substance these salts are reduced to violet metallic silver while silver sub-chloride is formed when pure silver chloride is exposed to light. The silver chloride paper, which has been darkened by light, is decolorized by hot nitric acid (the existence of free silver cannot be shown owing to the presence of organic matter which prevents the silver reaction).

"Still more intense is the coloring of silver chloride and silver bromide paper in presence of silver nitrate and ammonia. Silver chloride paper is colored a deeper shade than silver bromide paper; the latter becomes very dark when illuminated

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[1] Handbuch der Photographie, 4th Ed., 1, 172 (1890).

in presence of ammonia vapor (Schultz-Sellack). Silver iodide paper is only colored slightly grayish-yellow, and the color becomes brownish only after an exposure of a month or more.

"The modern silver positive process depends on the coloration by sunlight which silver chloride acquires when in presence of a silver salt and of an organic substance, especially paper. The usual sensitized positive paper of the photographers (albumen paper) contains, besides the substances mentioned, silver albuminate, an insoluble compound of albumen and silver salt which likewise turns very brown in the light and adds distinctly to the intensity and color of the picture....."

Further on in the same book Vogel[1] discusses the question of the effect of silver nitrate more in detail.

"While discussing the chemical behavior of the silver salts when exposed to light we mentioned the difference between the silver iodide obtained by precipitation with an excess of iodide and that obtained when silver nitrate solution is in excess. The latter is colored by light and the former not. From a photographic point of view, the two are also quite different. The first one, the one precipitated with an excess of potassium iodide, was considered for a long time to be photographically non-sensitive and this is certainly true for a dim light. Potassium iodide destroys the photographic sensitiveness of silver iodide almost completely; silver iodide which has been treated with a potassium iodide solution requires a very long exposure before it is possible to develop a picture.

"It is a fact however that the silver iodide obtained by precipitating with an excess of silver solution is photographically twenty times as sensitive as the other. If the silver solution, which covers the silver iodide, is saturated with organic substances like those resulting from the decomposition of collodion, then we find curiously enough that the

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[1] Handbuch der Photographie, 4th Ed., 1, 194 (1890).

silver iodide lacks sensitiveness to a surprising extent. According to earlier experiments of the author there is formed a double salt of silver iodide and silver nitrate which is much less sensitive to light than is silver iodide.

"According to experiments by the author silver bromide, precipitated by an excess of potassium bromide and washed carefully, is about one-fourth as sensitive as silver bromide precipitated from an excess of solution and also washed carefully.

"The substances, previously mentioned as combining with iodine, also have a favorable action on the photographic change of a collodion silver iodide. Silver iodide in contact with solutions of these substances is more sensitive to light than when pure. These substances are far inferior to silver nitrate solution in their sensitizing effect. Their sensitizing effect (for development) on the violet-sensitive silver bromide only shows when the latter salt has been precipitated in presence of an excess of potassium bromide. When silver bromide is precipitated from an excess of silver nitrate, is washed and dried, the effect of morphine, tannin, and such substances is rather harmful than beneficial. The reason for this is that these substances destroy the light traces of silver nitrate carried down by the silver bromide and substitute their own weak sensitizing action for that of silver nitrate, a substance *which has a much stronger sensitizing action than any of the organic substances.* Under these circumstances people have sometimes denied the sensitizing action of these substances.

"The sensitiveness of a photographic plate depends very largely on its opacity. The case may arise that a sensitizer does not act as such but actually makes a plate less sensitive by making it more transparent. If one wets half of a dry collodion silver iodide plate, it becomes much more transparent over the wetted portion and, after exposure, the developed plate is less dense on the wetted portion than on the dry portion. A similar effect is to be noticed when pyrogallol is used in solution. Poured on a dry silver iodide collodion film, it acts as a retarder and not as a sensitizer. The reason is that the chemically active rays pass through the solution in question without being absorbed. In consequence of this, people have often failed to notice the beneficial effect of sensitizers and even as late as 1870 Schultz-Sellack maintained that the *so-called sensitizers produce absolutely no effect.*"

The effect of depolarizers is brought out clearly by Eder's experiments[1] on aqueous solutions of chlorine and bromine to which were added citric acid or tartaric acid.

"Chlorine water and bromine water decompose gradually in the dark, the former more rapidly than the latter. In presence of tartaric acid or citric acid the decomposition of chlorine water and bromine water is accelerated both in the light and in the dark, but the rate of decomposition is much greater under the influence of light.

"Citric acid is attacked more readily by chlorine water, both in the light and in the dark than is tartaric acid. With bromine water the decomposition of these two acids takes place more slowly in the dark than with chlorine water, but in the sunlight the decomposition is about equally rapid with the two halogens.

"That the chemical energy of chlorine in light is increased more by presence of citric acid than of tartaric acid is shown by the following instance. Ferric chloride in presence of citric acid is more light-sensitive than in presence of tartaric acid, as Eder had shown previously.

"An alcoholic tincture of bromine is decolorized in a short time in the dark (half an hour to two hours). In direct sunlight the decolorization is almost instantaneous.

"The rate of photochemical decomposition of chlorine water, bromine water, and alcoholic iodine solution becomes less as the atomic weight of the halogen increases."

There are two things in this last quotation which might well have been worded differently. It is hardly correct to say that citric acid increases the chemical energy of chlorine;

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[1] Vogel: Handbuch der Photographie, 4th Ed., 1, 323 (1890).

it serves as a depolarizer and only as a depolarizer. The immediate connection between the chemical nature of the halogens and the rate of photochemical decomposition of their solutions is through their oxidizing powers and not through their atomic weights.

It would be a most instructive thing to determine decomposition voltages for all light-sensitive solutions. One would get in this way a pretty definite idea as to the direct current voltage of light. The problem might be complicated experimentally by the possibility of so-called excess voltages at the electrodes. When light acts on the solutions there are no electrodes and therefore no excess voltages of that type.

Grotthuss observed that ferric sulphocyanate was reduced by light to the ferrous salt under certain circumstances and that the ferrous salt was oxidized by light to the ferric salt under certain other circumstances. It is therefore necessary to consider under what conditions any given substance is reduced or oxidized by light. According to the theory of Grotthuss each ray of light is comparable to a linear voltaic cell. This means that a substance tends to be decomposed by all rays which are absorbed by it; but it does not tell in which direction the current is to run. Grotthuss was quite clear however that no reduction can take place without a simultaneous oxidation of something. Whether a given substance is to be reduced or oxidized by light depends therefore on the nature of the other substance (or substances) entering into the reaction. If the substance we are considering is in presence of a strong enough reducing agent, it will be reduced by light. If it is in presence of a strong enough oxidizing agent, it will be oxidized by light. When light is absorbed by mercurous chloride, the mercurous chloride tends to disappear; but there is nothing in the action of the light *per se* to determine whether the mercurous salt shall be reduced to mercury or shall be oxidized to a mercuric salt. Either change involves the elimination of the mercurous salt. In presence of ether, sunlight reduces mercurous chloride to mercury. In presence of an oxidizing agent, light changes mercurous chloride to mercuric salt. When no especial reducing agent is present, the mercurous chloride acts as its own depolarizer and we get a mixture of mercury and mercuric chloride. Light tends to set free chlorine from silver chloride and light causes silver and chlorine to react. In most cases of oxidation, the reaction takes place in presence of air and the oxidizing agent is oxygen. This was the case in the oxidation of ferrous sulphocyanate studied by Grotthuss. Many other cases are known and I quote two paragraphs in regard to it,[1] without in any way vouching for the accuracy of the observations quoted.

"Light accelerates many oxidation processes. Metals, especially lead, arsenic and antimony, oxidize more rapidly in sunlight according to Schönbein. Mercurous oxide is colored red in red light, taking up oxygen; violet light destroys the red color again (Davy). Since the reaction takes place also in a vacuum (Becquerel), there is probably a change to metallic mercury and mercuric oxide. Lead oxide, especially when prepared in the wet way, becomes gradually darker yellow, orange and brown when exposed to light (Schönbein); this change takes place only in presence of oxygen but not in a vacuum or in hydrogen, red lead being formed (Becquerel). This change takes place more readily in presence of alkali (Levol). In red light the oxidation takes place more rapidly than in violet light (Davy). According to Schönbein (1850) lead sulphide in thin layers is oxidized rapidly by light to lead sulphate and Schönbein actually obtained photographic copies by decolorizing lead sulphide paper. In 1852 Steinheil also obtained copies in the same way...."

"Ferrous sulphate is oxidized more rapidly in red light (= 1.2 to 1.6) and less rapidly in violet light (0.1–0.6) than in the dark (= 1.0). Ferrous hydroxide and manganous hydroxide behave similarly (Chastaing). In presence of air

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[1] Eder: Handbuch der Photographie, 2nd Ed., 1, 160 (1892).

metallic arsenic in dilute caustic potash solution is oxidized in the dark at a rate = 1.00; in violet light at a rate = 0.93 to 1.00; in red light at a rate = 1.04 to 1.20; and in green light at a rate = 1.00. Arsenious acid in dilute alkaline solution is also oxidized more rapidly in red light and less rapidly in violet light than in the dark (Chastaing). Dilute aqueous hydrogen sulphide is oxidized most rapidly in red light; sodium sulphide shows a different rate of precipitation of sulphur and hyposulphite in the light, red light accelerating the oxidation the most. Aqueous sulphurous acid in presence of air is oxidized to sulphuric acid chiefly by violet light (Chastaing); in the absence of air there is a decomposition into sulphur and sulphuric acid (Moren, Loew, Chastaing). Sulphites are not light-sensitive when not in contact with air."

Herschel's work on blue-print[1] paper is interesting for itself and also for its bearing on the theory of Grotthuss. If this theory had been known to Herschel, it seems probable that he would have seen the full bearing of it and that the development of photochemistry would have been quite different from what has actually been the case. I quote Herschel's experiments in full.

202. I shall conclude this part of my subject by remarking on the great number and variety of substances which, now that attention is drawn to the subject, appear to be photographically impressible. It is no longer an insulated and anomalous affection of certain salts of silver and gold, but one which, doubtless, in a greater or less degree pervades all nature, and connects itself intimately with the mechanism by which chemical combination and decomposition is operated. The general instability of organic combinations might lead us to expect the occurrence of numerous and remarkable cases of this affection among bodies of this class, but among metallic and other elements inorganically arranged, instances enough have already appeared, and more are daily presenting them-

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[1] Herschel: Phil. Trans., 132, 201 (1842).

selves, to justify its extension to all cases in which chemical elements may be supposed combined with a certain degree of laxity, and so to speak, in a state of tottering equilibrium. There can be no doubt that the process, in a great majority if not all the cases which have been noticed among inorganic substances is a deoxidizing one, so far as the more refrangible rays are concerned. It is obviously so in the case of gold and silver. In that of the bichromate of potash it is most probable that an atom of oxygen is parted with, and so of many others. A beautiful action of such deoxidizing action on a non-argentine compound has lately occurred to me in the examination of that interesting salt, the ferro-sesquicyanuret of potassium, described by Mr. Smee in the *Philosophical Magazine*, No. 109, September, 1840, and which he has shown how to manufacture in abundance and purity by voltaic action on the common or yellow ferrocyanuret. In this process nascent oxygen is absorbed, hydrogen given off, and the characters of the resulting compound in respect of the oxides of iron, forming as it does Prussian blue with proto-salts of that metal, but producing no precipitate with its per-salts, indicate an excess of electronegative energy, a disposition to part with oxygen, or, which is the same thing, to absorb oxygen (in the presence of moisture), and thereby to return to its pristine state, under circumstances of moderate solicitation, such as the affinity of protoxide of iron (for instance) for an additional dose of oxygen, etc.

203. Paper simply washed with a solution of this salt is highly sensitive to the action of light. Prussian blue is deposited (the base being necessarily supplied by the destruction of one portion of the acid, and the acid by the decomposition of another). After half an hour or an hour's exposure to sunshine, a very beautiful negative photograph is the result, to fix which all that is necessary is to soak it in water in which a little sulphate of soda is dissolved, to ensure the fixity of the Prussian blue deposited. While dry, the impression is dove-color or lavender blue, which has a curious and striking effect on the greenish yellow ground of the paper

produced by the saline solution. After washing, the ground color disappears and the photograph becomes bright blue on a white ground. If too long exposed it gets "oversunned" and the tint has a brownish or yellowish tendency, which however is removed in fixing; but no increased intensity beyond a certain point is obtained by continuance of exposure.

204. Prismatic examination of this process demonstrates the remarkable and valuable fact, that the decomposition of salt and deposit of Prussian blue is due to the action of the blue and violet rays, the less refrangible rays below the blue having absolutely no effect either to exalt or diminish the effect. The limits of action are about +18.0 and +61.0 fading insensibly both ways. [In the units used by Herschel the visible spectrum extended from —13.30 to +40.62 measured from a fiducial point or centre corresponding to the mean yellow ray.] The greatest intensity of action is at +38. A feebler maximum occurs at +23. The intensity of the action is much increased by washing with acidulated water, still more if it hold in solution a little persalt of iron, but in this case the ground, if not very carefully defended from light, is blue.

205. If a solution of this salt, mixed with perchloride of iron in a certain proportion be washed over paper somewhat bibulous and exposed to the spectrum, a copious and intense deposit of Prussian blue takes place over the region indicated in the last article. But it does not terminate here. On the contrary, the action is continued downwards in the spectrum, not only down to and beyond the extreme red rays but far below, *down to the very end of the thermic spectrum* (as far as the spot[1] called δ in Art. 136, and even with some traces of the more remote spot ϵ). The formation of the deposited colour in this region is accompanied with very singular phenomena, referable obviously to the heat developed by the thermic

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[1] [The spectrum was made by passing the light through a flint-glass prism. Five spots of special intensity were found in the infra-red. The names and approximate positions of these spots on the arbitrary scale are: α at —18.2; β at —26.7; γ at —45.1; δ at —45.2; and ϵ at —55.5.]

spectrum. Soon after the blue train, *ab*, Fig. 9,[1] in the positive region of the spectrum is formed, and has begun to acquire some intensity, an oval α, blunt at one extremity and pointed at the other, and of a dark brown colour, begins to appear. It enlarges rapidly, and at the same time throws forth a projection β indicating the action of that portion of the thermic spectrum so characterized in Art. 136. It also acquires a whitish narrow border indicated by the dotted line, and very conspicuous on the green ground of the paper. The action continuing, the spot γ is marked out by the extension of the border in that direction, soon after which the spot appears in brown. Lastly appears δ with feeble traces of further irregular and interrupted action. Measurements of these spots as they appear, leave no doubt of their identity in situation with the thermic spots α, β, γ, δ of Art. 136, and that they are referable to the drying of the paper is shown by the fact that a film of the liquid dried in a porcelain saucer changes from green to dark brown at a definite point of dryness. Moreover, on wetting the paper, the brown spots disappear, and in their place we find a train of Prussian blue, of varying intensity, but *of uniform breadth* (not swelling and contracting, as is the case with the heat-spots formed by simple drying and *therefore* obviously due to *direct* radiation), and terminating in two insulated and tolerably well-defined circular spots on solar images, holding precisely the place of γ and δ (*viz.*, at —35.7 and —45.1).

206. If in lieu of the perchloride of iron, we substitute a solution of that curious salt the *ammonia-citrate of iron*, the photographic effects are among the most various and remarkable that have yet offered themselves to our notice in this novel and fertile field of inquiry. The two solutions mix without causing any precipitate, and produce a liquid of a brown colour, which washed over paper is green (being strongly dichromatic). If this be done under the prism, the action of the spectrum is almost instantaneous, and most intense. A copiously and richly coloured deposit of Prussian

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[1] [Not reproduced in this article.]

blue is formed over the whole of the blue, violet, and extraspectral rays in that direction, extending downwards (with rapid graduation) almost to the yellow. If arrested when the blue is most intense and thrown into water, the impression is fixed; but if the action of the light be continued, strange to say, the blue and violet rays begin to destroy their own work. A *white* oval makes its appearance in the most intense part of the blue, which extends rapidly upwards and downwards. At a certain point of the action, the upper or more refrangible extremity of the white impression exhibits a semicircular termination, beyond which is a distinct and tolerably well-defined *conjugate image*, or insulated circular white spot, whose centre is situated far beyond the extreme visible violet.

207. If paper washed over with the mixed solution in question is exposed wet to sunshine, it darkens to a livid purple and rapidly whitens again. If the exposure be continued, the white again darkens gradually to a brownish violet hue. But in the shade it slowly resumes its original tint, after which it is again and again susceptible of the same round of action. The most singular and apparently capricious varieties of coloration and discoloration, however, arise (as is so frequently the case in photographic experiments) from different dosage of ingredients, order of washes, etc., so as to make the study of the phenomena in a high degree complicated.[1] A certain adjustment of proportions gives an exquisite and highly sensitive *positive* photographic paper; another, a negative one, in which the impression of light, feeble at first, is strongly brought out afterwards by an additional wash of the ferrosesquicyanuret, etc.

208. The ordinary ferrocyanuret (the yellow salt) though not nearly so sensible to photographic action of fixing against

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[1] The whitening is very obviously due to the deoxidation of the precipitated Prussian blue and the formation of the photo-ferrocyanuret of iron; the resumption of colour in the shade, to the reoxidizement of the compound, which is well-known to absorb oxygen from the air with avidity. Simple Prussian blue, however, is not whitened by the violet rays. Its state must be peculiar. (See postscript.)

the further action of light, and ultimately destroying photographic impressions on argentine papers. In conjunction also with preparations of silver, it has been made by Mr. Hunt the basis of a highly sensitive photographic paper. Its habitudes *per se*, are, however, not a little remarkable. Paper simply washed with its fresh solution and exposed to the spectrum, slowly receives a deposit of Prussian blue over the region of the blue, violet, and "lavender" rays, but this never becomes intense; another series of changes commencing, indicated by the formation of a violet-coloured streak within the blue, just where the violet itself is most intense in the spectrum. If the solution be very feebly acidulated with sulphuric acid, the first portion only of the spectral impression (from +13.3 to +20.0) is blue, the whole of the remainder (extending +51) snuff brown. The dose of acid being increased, the exposure prolonged, and the liquid plentifully supplied, a green thermic impression is produced by the less refrangible rays, in which the spots α, β, γ are very distinct, and lie exactly (by measure) in their proper places. This impression continues as far as the zero point where it begins to pass into blue, and graduates insensibly into the photographic spectrum, which attains its maximum of blue at +25, and is thence prolonged onwards as a dull bluish streak on a brown ground, somewhat broader than itself, and projecting like a border on both sides.

209. If paper be washed with a solution of ammonia-citrate of iron and dried, and then a wash passed over it of the yellow ferrocyanuret of potassium, there is no immediate formation of true Prussian blue, but the paper rapidly acquires a violet purple colour, which deepens after a few minutes, as it dries, to almost absolute black. In this state it is a positive photographic paper of high sensibility, and gives pictures of great depth and sharpness, but with this peculiarity, that they darken again spontaneously on exposure to air in darkness and are soon obliterated. The paper, however, remains susceptible to light and capable of receiving other pictures, which in their turn fade, without any possi-

bility (so far as I can see) of arresting them, which is to be regretted, as they are very beautiful, and the paper of such easy preparation. If washed with ammonia or its carbonate, they are for a few moments entirely obliterated, *but presently reappear with reversed lights and shades.* In this state they are fixed, and the ammonia, with all that it will dissolve, being removed by washing in water, their colour becomes a pure Prussian blue, which deepens much by keeping. If the solutions be mixed there results a very dark violet-coloured ink, which may be kept uninjured in an opaque bottle and will readily furnish, by a single wash, at a moment's notice, the positive paper in question, which is most sensitive when wet.

210. It seems at first sight natural to refer these curious and complex changes to the instability of the cyanic compounds, and that this opinion is to a certain extent correct, is proved by the photographic impressions described in Arts. 204 and 209, and where no iron is added beyond what exists in the ferrocyanic salts themselves. Nevertheless the following experiments abundantly prove that in several of the changes above described, the *immediate action* of the solar rays is not exerted on these salts but on the iron contained in the ferruginous solution added to them, which it deoxidizes or otherwise alters, thereby presenting it to the ferrocyanic salts in such a form as to precipitate the acids in combination with the peroxide or the protoxide of iron. To make this evident, all that is necessary is *simply to leave out the ferrocyanate* in the preparation of the paper, which thus becomes reduced to a simple washing over with ammonia-citric solution. Paper so washed is of a bright yellow colour, and is apparently little, but in reality highly sensitive to photographic action. Exposed to strong sunshine for some time indeed, its bright yellow tint is dulled into an ochrey hue, or even to gray, but the change altogether amounts to a moderate percentage of the total light reflected, and in short exposures is such as would easily escape notice. Nevertheless, if a slip of this paper be held for only four or five seconds

in the sun (the effect of which is quite imperceptible to the eye), and when withdrawn into the shade be washed over with the ferrosesquicyanate of potash, a considerable deposit of Prussian blue takes place on the part sunned, and none whatever on the rest, so that washing the whole with water, a pretty strong blue impression is left, demonstrating the reduction of iron in that portion of the paper to the state of protoxide. The effect in question is not, it should be observed, peculiar to the ammonia-citrate of iron. The ammonio—and potassium—tartrate fully possess, and the perchloride *exactly neutralized* partakes of the same property, but the experiment is far more neatly made and succeeds better with the other salts.

211. If a long strip of paper, prepared as in the last article, be marked off into compartments and subjected to graduated exposure to sunshine, so that the times of exposure in each succession shall form an arithmetical progression of 1, 2, etc., and when withdrawn washed over as aforesaid with the ferrosesquicyanuret and rinsed in water, the blue deposit is found to increase with the time of exposure up to a very deep and full colour, after which its total intensity, so far from increasing, diminishes, and at length almost vanishes. Again, if a slip of the same paper be exposed a long while to the spectrum, the whole impression consists in a feeble ochrey-brown streak extending over the region of the blue, violet and lavender rays as far as about +55. But on the application of the cyanic solution (in the shade) a most intense blue spectrum is developed over the whole of the more refrangible region, in the interior of which the blue colour appears to have been, as it were, eaten away, leaving a white oval, as in the specimen annexed, precisely the same phenomenon, in short, as would have been produced under the spectrum had the two liquids acted in conjunction. And this white portion comports itself under the influence of water or air, just as it would have done had it been produced under such joint action; *i. e.*, it gradually turns blue till it is no longer distinguishable from the rest of

the spectrum. It is also blued by ammonia, just as the positive paper of Art. 210, after bleaching would be. In short, it is evident that we have succeeded in separating the final action described in that article into two distinct steps or stages, the photographic influence being confined to the first, and the ferrosesquicyanate as a mere precipitant on the nascent compounds resulting from that influence.

212. In order to ascertain whether any portion of the iron in the double ammoniacal salt employed had really undergone deoxidation, and become reduced to the state of protoxide as supposed, I had recourse to a solution of gold, exactly neutralized by carbonate of soda. The proto-salts of iron, as is well-known to chemists, precipitate gold in the metallic state. The effect proved exceedingly striking, issuing in a process in no wise inferior in the almost magical beauty of its effect to the calotype process of Mr. Talbot, which in some respects it nearly resembles, with this advantage, as a matter of experimental exhibition, that the disclosure of the dormant image does not require to be performed in the dark, being not interfered with by moderate daylight. As this experiment will probably be repeated by others, I shall here describe it *ab initio.* Paper is to be washed with a moderately concentrated solution of ammonio-citrate of iron, and dried. The strength of the solution should be such as to dry into a good yellow colour, not at all brown. In this state it is ready to receive a photographic image, which may be impressed on it either from nature in the camera-obscura, or from an engraving on a frame in sunshine. The image so impressed, however, is very faint, and sometimes hardly perceptible. The moment it is removed from the frame or camera, it must be washed over with a neutral solution of gold of such strength as to have about the colour of sherry wine. Instantly the picture appears, not indeed at once of its full intensity, but darkening with great rapidity up to a certain point, depending on the strength of the solutions used, etc. At this point nothing can surpass the sharpness and perfection of detail of the resulting photograph. To

arrest this process and to fix the picture (so far at least as the further agency of *light* is concerned), it is to be thrown into water very slightly acidulated with sulphuric acid and well soaked, dried, washed with hydrobromate of potash, rinsed, and dried again.

In a postscript added August 29, 1842, Herschel describes further experiments with iron salts.[1]

217. I gladly avail myself of the permission accorded to the President and Council to append to this communication, in the form of a postscript, some additional facts illustrative of the singular properties of iron as a photographic ingredient, which have been partially developed in the latter articles of it as well as an account of some highly interesting photographic processes dependent on those properties, which the superb weather we have lately enjoyed has enabled me to discover, as also to describe a better method of fixing the picture, in the process to which I have given the name of *Chrysotype*, that described in Art. 212 proving insufficient. The new method (in which the hydriodate is substituted for the hydrobromate of potash) proves perfectly effectual, pictures fixed by it not having suffered in the smallest degree, either from long exposure to sunshine, or from keeping; alone, or in contact with other papers. It is as follows: As soon as the picture is satisfactorily brought out by the auriferous liquid (Art. 212) it is to be rinsed in spring water, which must be three times renewed, letting it remain in the third water five or ten minutes. It is then to be blotted off and dried, after which it is to be washed on both sides with a somewhat weak solution of hydriodate of potash. If there be any free chloride of gold present in the pores of the paper, it will be discoloured, the lights passing to a ruddy brown, but they whiten again spontaneously, or at all events, on throwing it (after lying a minute or two) in fresh water, in which, being again rinsed and dried, it is now perfectly fixed.

218. If paper prepared as above recommended for the

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[1] Phil. Trans., 132, 209 (1842).

chrysotype, either with the ammonio-citrate or ammonio-tartrate of iron, and impressed, as in that process, with a latent picture, be washed with nitrate of silver instead of a solution of gold, a very sharp and beautiful picture is developed, of great intensity. Its disclosure is not instantaneous; a few moments elapse without apparent effect; the dark shades are then touched in, and by degrees the details appear, but much more slowly than in the case of gold. In two or three minutes, however, the maximum of distinctness will not fail to be attained. The picture may be fixed by the hyposulphite of soda, which alone, I believe, can be fully depended on for fixing argentine photographs.

219. *Cyanotype.* If a nomenclature of this kind be admitted (and it has some recommendations) the whole class of processes in which cyanogen in its combinations with iron performs a leading part, and in which the resulting pictures are blue, may be designated by this epithet. The varieties of cyanotype processes seem to be innumerable, but that which I shall now describe deserves particular notice, not only for its pre-eminent beauty while in progress, but as illustrating the peculiar power of the ammoniacal and other persalts of iron above mentioned to receive a latent picture, susceptible of development by a great variety of stimuli. This process consists in simply passing over the ammonio-citrated paper on which such a latent picture has been impressed, *very sparingly and evenly*, a wash of the solution of the common yellow ferrocyanate (prussiate) of potash.[1] The latent picture, if not so faint as to be quite invisible (and for this purpose it should not be so) is negative. As

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[1] Vulgarly, and in my opinion very conveniently and *correctly* so-called, according to the true intent and meaning of Scheele. Trivial names for common objects are to be maintained and depended on principles far more general than systematic nomenclature. For this reason I trust never to see the name muriatic give way to hydrochloric, or nitric thrust aside for azotic acid. The *prussic* acid is that acid, whatever it may be, which, united with oxide of iron as a base forms Prussian blue, from which remarkable compound the whole history of cyanogen originated. The now ascertained existence of another ferrocyanate makes this recurrence to a trivial name for the vulgar one more necessary now.

soon as the liquid is applied, which cannot be in too thin a film, the negative picture vanishes, and by very slow degrees is replaced by a positive one of a violet-blue colour on a greenish-yellow ground, which at a certain moment possesses a high degree of sharpness and singular beauty and delicacy of tint. If at this instant it be thrown into water, it passes immediately to Prussian blue, losing at the same time, however, much of its sharpness, and sometimes indeed becoming quite blotty and confused. But if this be delayed, the picture, after attaining a certain maximum of distinctness, grows rapidly confused, especially if the quantity of liquid applied be more than the paper can easily and completely absorb, or if the brush in applying it be allowed to rest on, or be passed twice over any part. The effect then becomes that of a coarse and ill-printed wood-cut, all the strong shades being run together, and a total absence prevailing of half lights.

220. To prevent this confusion, gum-arabic may be added to the prussiated solution by which it is hindered from spreading unmanageably within the pores of the paper, and the precipitated Prussian blue allowed time to agglomerate and fix itself on the fibres. By the use of this ingredient also, a much thinner and more equable film may be spread over the surface; and *when perfectly dry*, if not sufficiently developed, the operation may be repeated. By operating thus I have occasionally (though rarely) succeeded in producing pictures of great beauty and richness of effect, which they retain (if not thrown into water) between the leaves of a portfolio, and have even a certain degree of fixity—fading in a strong light and recovering their tone in the dark.

221. If sulphocyanate of potash be added to the ammonio-citrate or ammonio-tartrate of iron, the peculiar red colour which that test induces on persalts of the metal is not produced, but appears at once on adding a drop or two of dilute sulphuric or nitric acid. This circumstance, joined to the perfect neutrality of these salts, and their power, in such neutral solution, of enduring, undecomposed, a boiling

heat, contrary to the usual habitudes of the peroxide of iron,[1] together with their singular transformation by the light to proto-salts, in apparent opposition to a very strong affinity, has, I confess, inclined me to speculate on the possibility of their ferruginous base existing in them, not in the ordinary form of peroxide, but in one isomeric with it. The non-formation of Prussian blue when their solutions are mixed with prussiate of potash (Art. 209), and the formation in its place of a deep violet-coloured liquid of singular instability under the action of light seems to favor this idea. Nor is it altogether impossible that the peculiar "prepared" state superficially assumed by iron under the influence of nitric acid, first noticed by Keir, and since made the subject of experiment by M. Schönbein and myself,[2] may depend on a change superficially operated on the *iron itself* into a new metallic body isomeric with iron, unoxidizable by nitric acid, and which may be considered as the radical of that peroxide which exists in the salts in question, and possibly also of an isomeric protoxide. A combination of the common protoxide with the isomeric peroxide, rather than with the same metal in a simply higher stage of oxidation, would afford a not unplausible notion of the chemical nature of that peculiar intermediate oxide to which the name of "ferroso-ferric" has been given by Berzelius. If (to render my meaning more clear) we for a moment consent to designate such an isomeric form of iron by the name siderium, the oxide in question might be regarded as a sideriate of iron. Both phosphorus and arsenic (bodies remarkable for sesqui combinations) admit isomeric forms in their oxides and acids.[3] But to return from this digression.

222. If to a mixture of ammonio-citrate of iron and sulphocyanate of potash a small dose of nitric acid be added, the resulting red liquid spread on paper spontaneously whitens

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[1] See my paper on this subject in *Philosophical Transactions*, 111, 293.

[2] See Annales de Chimie, 54, 87.

[3] The latter from the late experiments and remarks of Rose on the vitreous state of the arsenious acid and its luminosity in crystallizing from acid solutions.

in the dark. If more acid be added till the point is attained when the discoloration begins to relax, and the paper when dry retains a considerable degree of colour, it is powerfully affected by light, and received a positive picture with great rapidity, which, like the guaiacum impression noticed in Art. 154, appears at the back of the paper with even more distinctness than on its face. The impression, however, is pallid; fades on keeping, nor am I acquainted at present with any mode of fixing it.

233. If paper be washed with a mixture of the solutions of ammonio-citrate of iron and ferrosesquicyanate of potash, so as to contain the two salts in about equal proportions, and being then impressed with a picture, be thrown into water and dried, a negative blue picture will be produced agreeably to what is stated in Art. 154. This picture I have found susceptible of a very curious transformation preceded by total obliteration. To effect this it must be washed with solution of proto-nitrate of mercury, which in a little time entirely discharges it. The nitrate being thoroughly washed out and the picture dried, a smooth iron is to be passed over it, somewhat hotter than is used for ironing linen, but not sufficiently so to scorch or to injure the paper. The obliterated picture immediately reappears, not blue, but brown. If kept for some weeks in this state between the leaves of a portfolio, in complete darkness, it fades, and at length almost disappears. But what is very singular, a fresh application of the heat revives and restores it to its full intensity.

224. This curious transformation is instructive in another way. It is not operated by light, at least not by light alone. *A certain temperature* must be obtained, and that temperature suffices in total darkness. Nevertheless, I find that on exposing to a very concentrated spectrum (collected by a lens of short focus) a slip of paper duly prepared as above (that is to say by washing with the mixed solutions, exposure to sunshine, and discharging the uniform blue colour so induced as in the last article), its whiteness is changed to brown over the whole region of the red and orange rays, *but not beyond*

the luminous spectrum. Three conclusions seem unavoidable: first, that it is the heat of these rays, not their light, which operates the change; secondly, that this heat possesses a purely chemical quality which is not possessed by the purely calorific rays outside of the visible spectrum though far more intense; thirdly, that the heat radiated from obscurely hot iron, abounds especially in rays analogous to those of the region of the spectrum above indicated. And these are the very same conclusions derived from the experiments on guaiacum in Art. 158-160.

225. Whatever be the state of the iron in the double salts in question, its reduction by blue light to the state of protoxide is indicated by many other reagents. If, for example, a slip of paper prepared with the ammonio-citrate and partially sunned, be washed, when withdrawn, with bichromate of potash, the bichromate is deoxidized and precipitated on the sunned portion, just as it would be if directly exposed to the sun's rays. Every reagent in short which is susceptible of being deoxidated, wholly or in part, by contact with the protoxide of iron, is so also by contact with the sunned paper. Taking advantage of this property, I have been enabled to add another and very powerful element to the list of photographic ingredients.

226. *Photographic Properties of Mercury.* This element is mercury. As an agent in the Daguerreotype process, it is not, strictly speaking, photographically affected. It operates there only in virtue of its readiness to amalgamate with silver, properly prepared to receive it. That it possesses *direct* photographic susceptibility, however, in a very eminent degree, is proved by the following experiment. Let a paper be washed over with a weak solution of periodide of iron, and when dry with a solution of protonitrate of mercury. A bright yellow paper is produced, which (if the right strength of the liquid be hit) is exceedingly sensitive while wet, darkening to a brown colour in a very few seconds in the sunshine. Withdrawn, the impression fades rapidly, and the paper in a few hours recovers its original colour. In operating this

change of colour the whole spectrum is effective, with the exception of the thermic rays beyond the red.

227. Protonitrate of mercury simply washed over paper is slowly and feebly blackened by exposure to sunshine. And if paper be impregnated with the ammonio-citrate, already so often mentioned, partially sunned, and then washed with the proto-nitrate, a reduction of the latter salt, and consequently the blackening of the paper takes place very slowly in the dark over the sunned portion, to nearly the same amount as in the direct action of the light on the simply nitrated paper.

228. But if the mercurial salt be subjected to the action of light in contact with the ammonio-citrate, or tartrate, the effect is far more powerful. Considering, at present, only the citric double-salt, a paper prepared by washing first with that salt and then with the mercurial proto-nitrate (drying between) is endowed with considerable sensibility, and darkens to a very deep brown, nay to complete blackness, on a moderate exposure to good sun. Very sharp and intense photographs of a negative character may be thus taken. They are, however, difficult to *fix*. The only method which I have found at all to succeed, has been by washing them with bichromate and soaking them for twenty-four hours in water, which *dissolves out* the chromate of mercury for the most part, leaving however a yellow tint on the ground which resists obstinately. But though pretty effectually fixed in this way against *light*, they are not so against *time*, as they fade considerably on keeping.

229. When the proto-nitrate of mercury is mixed, in solution, with either of the ammoniacal double salts, it forms a precipitate, which, worked up with a brush to the consistency of cream, is easily (and with certain precautions of manipulation)[1] very evenly spread on paper, producing photo-

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[1] The cream should be spread as rapidly as possible over the whole paper, well worked in, cleared off as much as possible, and finished with a brush nearly dry, spread out broad and pressed to a straight thin edge, which must be drawn as lightly and evenly as possible over every part of the paper till the surface appears free from every streak and barely moist.

graphic tablets of every variety of sensibility and inertness, according to the proportion of the doses used. By combining all three of the ingredients, and adding a small quantity of tartaric acid,[1] a paper is produced of a pretty high degree of sensibility (more than by the use of either separately) which in about half an hour, according to the sun, affords pictures of such force and depth of colour, such velvety richness of material, and such perfection of detail and preservation of the relative intensities of the light, as infinitely to surpass any photographic production I have yet seen, and which indeed it seems impossible to go beyond. Most unfortunately, they cannot be preserved. Every attempt to fix them has resulted in the destruction of their beauty and force; and even when kept from light, they fade with more or less rapidity, some disappearing almost entirely in three or four days, while others have resisted tolerably well for a fortnight, or even a month. It is to an overdose of tartaric acid that their more rapid deterioration seems to be due, and of course it is important to keep down the proportion of this ingredient as low as possible. But without it, I have never succeeded in producing that peculiar velvety aspect on which the charm of these pictures chiefly depends, nor anything like the same intensity of colour without oversunning.

These results become intelligible if we apply the theory of Grotthuss. By electrolysis of potassium ferrocyanide we get potassium ferricyanide and a blue precipitate. We get the same reaction under the influence of light. Electrolysis of potassium ferricyanide gives potassium ferrocyanide and a blue precipitate. The action of light produces the same result. The reaction is accelerated by the presence of sugar or potassium oxalate. According to Vogel substances dyed with Prussian blue are bleached by light, the blue colour re-

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[1] One measure of a solution of ammonio-citrate, and one of a solution of ammonio-tartrate of iron, containing, each one-tenth of its weight of the respective salts. Tartaric acid, saturated solution, one-eighth of the *joint volumes* of the other solutions. Form a cream by pouring in as rapidly as possible one measure of a saturated solution of the proto-nitrate and well mixing with a brush.

turning in the dark. Vogel attributes the reversion to the blue color as resulting from the formation of a basic salt. It seems more probable that the bleaching is due to a reduction to ferrous ferrocyanide or potassium ferro-ferrocyanide, $K_2FeFe(CN)_6$, this salt then being oxidized again when removed from the light.

In Herschel's first experiments he used paper impregnated with potassium ferricyanide and obtained a blue negative. With a paper impregnated with a mixture of potassium ferricyanide and ferric chloride, the ferric salt is reduced first and Turnbull's blue is formed. The brown color on further exposure to light is due to the formation of an apparently unknown compound. We know that the substance can be formed by chemical reduction of Prussian blue and there is therefore no inherent reason why it should not be formed by the action of light or of electricity.[1] The difference between this case and the next one with the double ammonium citrate is that we have here an excess of a ferrous salt which would naturally be favorable to the formation of a substance high in iron.

In the next set of experiments, the double ferric ammonium citrate and potassium ferricyanide were added to the paper. The sunlight sets free ferrous salt from the citrate and forms Prussian blue. The further action of light is to generate the white ferrous ferrocyanide or potassium ferro-ferrocyanide which is oxidized back to Prussian blue when left in the dark. At first sight it appears as though the ferrous ferrocyanide were obtained by the direct action of the light on ferrous ferricyanide. This is probably not what happens in this particular case. In a later experiment, Herschel saturated the paper with the double citrate solution and added the ferricyanide only after the exposure to sunlight had been made. Under these circumstances he got precisely the same result as when the mixture of the salts was exposed, namely a blue in the parts exposed a short time

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[1] Since this passage was first written, Mr. Schluederberg has succeeded in getting first the white and then the brown electrolytically.

to light, and a white spot where intense light had acted for a long time. From this we must conclude that the action of light on paper impregnated with the double ammonium ferric citrate, if continued long enough, gives rise to ferrous salt and to a reducing agent powerful enough to reduce ferricyanide at once to ferrocyanide. Since we get a reversal of color on exposing long enough, it is clear that we can get either a positive or a negative depending on the conditions, and this was what Herschel found. On the other hand, one would suppose from the text that the positive was more sensitive than the negative, and it is difficult to see how this can be so. Since Herschel does not give his exact conditions it is impossible to duplicate his results.

Starting with ferrocyanide of potash alone Herschel obtained a blue negative as was to be expected. Further exposure caused the appearance of a violet-colored streak which turned brown on treating with a few drops of sulphuric acid. Here again we are probably dealing with the formation of an unknown compound and here again it is our knowledge of chemistry that is at fault.

When paper is washed with a double citrate solution and with a ferrocyanide solution, the action of light produces white ferrocyanide and we get a positive. These will absorb oxygen from the air, will darken spontaneously, and will be in a state to have new pictures formed by the action of light. Since ferrous salts oxidize very rapidly in alkaline solutions, we shall get a rapid oxidation to ferric ferrocyanide if we add ammonia. The white lines will change to blue and the lights and shades will be reversed, just as Herschel found experimentally.

In the experiment with the double citrate and potassium sulphocyanate (Art. 222), just enough nitric acid is added to prevent the ferric sulphocyanate from being reduced spontaneously in the dark. The light turns the scale and causes a reduction. The principle involved is the same as in the experiments with ferric sulphocyanate made by Grotthuss.

The fact that no ferric sulphocyanate is formed when potassium sulphocyanate is added to a neutral ammonium ferric citrate or ammonium ferric tartrate ceases to excite surprise now that we distinguish between a double salt and a complex salt. In a sense, however, Herschel's explanation is not so far wrong. The difference between the properties of two allotropic forms are no greater than the difference between the properties of iron as ion and as part of the citrate or tartrate radical. It is also interesting to note that within the last few years Herschel's explanation of the passivity of iron as due to an allotropic modification has been defended at length.

My knowledge of the chemistry of mercury salts is not sufficient to enable me to account for all of Herschel's results with mercuric nitrate, but I see no reason to suppose that the photochemical reactions will present any serious difficulties and I shall hope to report on this in the near future."

III. OXIDATION OF ORGANIC COMPOUNDS

The most important oxidizing action of light is in the changing of organic materials and dyestuffs. We do not know whether the same products are always obtained by electrolytic oxidation and by the action of sunlight and air; and that is a point which will have to be studied with care. We have a reducing agent, the organic substance, and an oxidizing agent, oxygen. The conditions are therefore favorable for a decomposition by light. Whether we are to consider the oxygen as the depolarizing substance, or the dye as the depolarizer, or whether each acts as a depolarizer to the other, is a question to be decided experimentally in each particular case. Bredig[1] appears to have answered the question in one way for certain reactions. As I have never seen the original article I quote a review of it.[2]

"The authors start with the assumption that oxygen is made chemically more active by a radiation which increases its electrical conductivity. Since there is a question whether

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[1] Bredig and Pemsel: Arch. wiss. Photographie, 1, 33 (1899).

[2] Beiblätter, 23, 795 (1899).

light makes the oxidizing oxygen or the substance to be oxidized more ready to react, they then made the experiment of submitting the air alone to the radiation and determining whether the air immediately afterwards reacted more rapidly with the substance to be oxidized. As an oxidizable substance a dilute solution of sodium sulphite was taken because Bigelow had shown that its rate of oxidation is affected markedly by the slightest disturbances. Although the air kept its electrical conductivity for an appreciable time after being exposed to X-rays or uranium rays, the results were absolutely negative and no increase in the rate of oxidation could be detected analytically after a separate exposure to different radiations."

In another review,[1] it is stated that no acceleration was observed after exposure to ultra-violet light and that the authors conclude that the increased reaction velocity is due to the light making the substance to be oxidized more active. While it is probable that the conclusions of the authors are correct for this particular case, it does not seem to me that their reasoning is sound. From neither of these reviews does it appear that they tried the reverse experiment of submitting the sodium sulphite solution to radiation and afterwards passing in air. It is probable that such an experiment would also have yielded a negative result and reasoning from that alone one would have concluded that it was the oxygen which was made active by light. Since ultra-violet light converts oxygen into ozone, the negative results with air and ultra-violet light can only be due to some peculiarity in the experiments which prevented the formation of ozone. Ultra-violet light is a fairly elastic term and the authors may have used light of such wave-length or intensity that no ozone was formed.

While the experiments of Bredig and Pemsel, as judged from the two reviews, do not appear to warrant the conclusions drawn from them, there is one conclusive way of determining the question. If the active light is light which

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[1] Zeit. Elektrochemie, 6, 137 (1899).

is absorbed by the substance to be oxidized and not by the oxygen, then the substance to be oxidized has been made active by the light and the oxygen is the depolarizer. If the active light is absorbed by oxygen and not by the substance to be oxidized, then this latter is the depolarizer and the oxygen is made active by light. If the active light is absorbed by both, it is possible that each is made active and that each is also the depolarizer. In this last case, however, the results should be checked by experiments with another oxidizing agent and another reducing agent. While light can only act in case it is absorbed it does not follow that all light which is absorbed acts to any appreciable extent. In the bromination of organic compounds,[1] the most effective rays are those corresponding to the weaker bromine absorption bands in the yellow-green and orange, instead of those corresponding to the stronger absorption bands in the greenish-blue and blue.

If we apply the test of the active light to many of the cases, we shall find that the conclusions of Bredig and Pemsel hold in most cases. In the cases of oxidation by light previously quoted, the acceleration was usually greater in red light than in violet. Since the ozone formation takes place under the influence of ultra-violet light, it is safe to conclude that the oxygen acts merely as a depolarizer in these cases. The following experiments of Herschel[2] on the action of light on the coloring matter of flowers show that it is the coloring matter which is made active by the sun's rays.

169. The action of the spectrum, or of white light, on the colours of flowers and leaves, is extremely various, both as regards its total intensity and the distribution of the active rays over the spectrum. But certain peculiarities in this species of action obtain almost universally.

(1) The action is *positive*, that is to say, light destroys colour; either totally, or leaving a residual tint, on which it has no further, or a very much slower action. And thus is

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[1] Schramm and Zakrzewski: Monatsheft, 8, 299 (1897).

[2] Phil. Trans., 132, 181 (1842).

effected a sort of chromatic analysis, in which two distinct elements of colour are separated, by destroying the one and leaving the other outstanding. The older the paper, or the tincture with which it is stained, the greater is the amount of this residual tint.

(2) The action of the spectrum is confined, or nearly so, to the region of it occupied by the luminous rays, as contradistinguished both from the so-called chemical rays beyond the violet, which act with chief energy on argentine compounds, but are here for the most part ineffective, on the one hand, and on the other, from the thermic rays beyond the red, which appears to be totally so. Indeed, I have hitherto observed no instance of the extension of this description of photographic action on vegetable colours beyond or even *quite* up to the extreme red.

170. Besides these, it may also be observed that the rays effective in destroying a given tint are, in a great many cases, those whose union produces a colour complementary to the tint destroyed, or at least one belonging to that class of colours to which such complementary tint may be referred. For example, yellows tending toward orange are destroyed with more energy by the blue rays; blues by the red, orange and yellow rays; purples and pinks by yellow and green rays.

171. These are certainly remarkable and characteristic peculiarities, and must indeed be regarded as separating the luminous rays by a pretty broad line of chemical distinction from the non-luminous; though whether they act *as such*, or in virtue of some peculiar chemical quality of the heat which accompanies them *as heat*, is a point which the experiments on guaiacum, above described, seem to leave rather equivocal. In the latter alternative, chemists must henceforward recognize differences not simply of intensity, but of quality in heat from different sources; of quality, that is to say, not merely as regards degree of refrangibility or transcalescence, but as regards the strictly chemical changes it is capable of effecting in ingredients subjected to its influence.

172. As above stated, these peculiarities, at least the first two, obtain almost universally. Exceptions, however, though very rare, do occur, as will be more particularly mentioned hereafter. The third rule is much less general, and is to be interpreted with considerable latitude, but among its exceptions I have been unable to detect any common principle capable of being distinctly enunciated.

177. *Common ten-weeks Stock, Mathiola Annua.* The colour imparted by the petals of the *double variety* of this flower[1] to alcohol (at least when spread on paper, for it is in great measure dormant in the liquid tincture) is a rich and florid rose-red, varying, however, from a fiery tint almost amounting to scarlet, on the one hand, to a somewhat crimson or purplish red on the other, according to the accidents of its preparation, or the paper used. When freshly prepared it is considerably sensitive, an hour or two of sunshine being sufficient to produce a sensible discoloration, and two or three days entirely to whiten it. This quality is greatly deteriorated by keeping, but papers prepared with it even after eight or ten months, still with patience yield extremely beautiful photographs, several specimens of which in various states of the tincture are submitted for inspection to the meeting exposed to the spectrum; the rays chiefly active in operating the discoloration are found to be those extending from the yellow to the less refrangible red, beyond which rays the action terminates abruptly. Above the yellow it degrades rapidly to a minimum in the blue beyond which it recovers somewhat, and attains a second but much feebler maximum in the violet rays.

178. Paper stained with the tincture of this flower is changed to a vivid scarlet by acids, and to green by alkalies; if ammonia be used the red colour is restored as the ammonia evaporates, proving the absence of any acid quality in the colouring matter sufficiently energetic to coerce the elastic

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[1] That imparted by the single flowers is very much less sensitive, as is also that of the dull or purplish variety, whether double or single. The most florid red double flowers in the height of their flowering yield the best color

force of the alkaline gas. Sulphurous acid whitens it, as do the alkaline sulphites, but this effect is transient, and the red colour is slowly restored by free exposure to air, especially with the aid of light, whose influence in this case is the more remarkable, being exactly the reverse of its ordinary action on this colouring principle, which it destroys irrecoverably, as above stated. The following experiments were made to trace and illustrate this curious change.

179. Two photographic copies of engravings taken on paper tinted with this colour were placed in a jar of sulphurous acid gas, by which they were completely whitened, and all traces of the pictures obliterated. They were then exposed to free air, the one in the dark, the other in sunshine. Both recovered, but the former much more slowly than the latter. The restoration of the picture exposed to sun was completed in twenty-four hours, that in the dark not till after a lapse of two or three days.

180. A slip of the stained paper was wetted with liquid sulphurous acid and laid on blotting paper similarly wetted. Being then crossed with a strip of black paper, it was laid between glass plates and (evaporation of the acid being thus prevented) was exposed to full sunshine. After some time the red colour (in spite of the presence of the acid) was considerably restored in the portion exposed, while the whole of the portion covered by the black paper remained (of course) perfectly white.

181. Slips of paper, stained as above, were placed under a receiver, beside a small capsule of liquid sulphurous acid. When completely discolored they were subjected (on various occasions, and after various lengths of exposure to the acid fumes from half an hour to many days) to the action of the spectrum; and it was found, as indeed I had expected, that *the restoration of colour was operated by rays complementary to those which destroy it in the natural state of the paper*, the violet rays being chiefly active, the blue almost equally so, the green little, and the yellow, orange, and most refrangible red not at all. In one experiment a pretty well-defined red

solar image was developed by the *least* refrangible red rays also, being precisely those for which in the unprepared paper the discoloring action is abruptly cut off. But this spot I never succeeded in reproducing; and it ought also to be mentioned, that, according to difference in the preparation not obvious, the degree of sensibility, generally, of the bleached paper to the restorative action of light differed greatly, in some cases perceptible reddening being produced in ten seconds, and a considerable streak in two minutes, while in others a very long time was required to produce any effect.

182. The dormancy of this colouring principle, under the influence of sulphurous acid, is well shown by dropping a little weak sulphuric acid on the paper bleached by that gas, which immediately restores the red colour in all its vigour. In like manner alkalies restore the colour, converting it at the same time into green.

183. *Papaver Orientale.*—The chemical habitudes of the sulphurous acid render it highly probable that its action, in inducing a dormant state of the colorific principle, consists in a partial deoxidizement, unaccompanied however with disorganization of its molecules. And this view is corroborated by the similar action of alcohol already spoken of; similar, that is, in kind though less complete in degree. Most commonly, vegetable colours, weakened by the action of alcohol, are speedily restored on the total evaporation of that ingredient. But one remarkable instance of absolute dormancy induced by that agent, has occurred to me in the case of the *Papaver orientale*, a flower of a vivid orange colour, bordering on scarlet, the colouring matter of which is not extractable otherwise than by alcohol, and then only in a state so completely masked, as to impart no more than a faint yellowish or pinkish hue to paper, which it retains when thoroughly dry, and apparently during any length of time without perceptible increase of tint. If at any time, however, a drop of weak acid be applied to paper prepared with this tincture, a vivid scarlet colour is immediately developed, thus demonstrating the continued though latent existence of the colour-

ing principle. On observing this, it occurred to me to inquire whether, in its dormant state, that principle still retained its susceptibility of being acted on by light, since the same powerful and delicate agent which had been shown, in so many cases as to constitute a general law, capable of disorganizing and destroying vegetable colours actually developed, might easily be presumed competent to destroy the capacity for assuming colour, in such organic matter as might possess it, under the influence of their otherwise appropriate chemical stimuli. A strip of the paper was therefore exposed for an hour or two to the spectrum, but without any sensible effect, the whole surface being equally reddened by an acid. As this experiment sufficiently indicated the action of light, if any, to be very slow, I next placed a strip, partly covered, in a southeast window, where it remained from June 19th to August 19th, receiving the few and scanty sunbeams which that interval of the deplorable summer of 1841 afforded. When removed, the part exposed could barely be distinguished from the part shaded, as a trifle yellower. But on applying acid, the exposed and shaded portions were at once distinguished by the assumption of a vivid red in the latter, the former remaining unchanged.

184. A mezzotinto picture was now pressed on a glazed frame over another portion of the same paper, and abandoned on the upper shelf of a greenhouse to whatever sun might occur from August 19th to October 19th. The interval proved one of almost uninterrupted storm, rain, and darkness. On removal, no appearance whatever of any impressed picture could be discerned, nor was it even possible to tell the top of the picture from the bottom. It was then exposed in a glass jar to the fumes of muriatic acid, when, after a few minutes, the development of the dormant picture commenced, and slowly proceeded disclosing the details in a soft and pleasing style. Being then laid by in a drawer, with free access of air, the picture again faded, by very slow degrees, and on January 2, 1842, was found quite obliterated. Being then again subjected to the acid vapour, the colour

was reproduced. How often this alternation might have gone on, I cannot say, the specimen having been mislaid or destroyed; but a portion of such paper photographically impressed with a stamped pattern, accompanies this communication for the satisfaction of any member who may wish to try the experiment. The extreme slowness of the action precludes any prismatic analysis of the process and it cannot be too often repeated *that the use of colored glasses in such inquiries serves only to mislead.* Of dormant photographic impressions generally, whether slowly developing themselves by lapse of time, or at once revivable by stimuli, as well as of the spontaneous fading and disappearance of such impressions, I shall have more to say hereafter, having encountered several very curious cases of the kind in studying the habitudes of gold, plating, etc. I would here only observe that a consideration of many such phenomena has led me to regard it as not impossible that the retina itself may be *photographically* impressible by strong lights, and that some at least of the phenomena of visual spectra and secondary colours may arise from the sensorial perception of actual changes in progress in the physical state of the organ itself subsequent to the cessation of the direct stimulant.

These two cases are quite simple in the light of the Grotthuss theory. The coloring matter of the stocks is such a weak acid that the color is changed only by an excess of ammonia and returns as the ammonia evaporates. The coloring matter also forms a colorless compound with the sulphurous acid or with sulphites. The sulphite part of the new compound is evidently more readily oxidized than the organic extract and consequently the first action of the light is to oxidize the sulphite to sulphate, regenerating the original color. While some of the rays that are absorbed by the sulphite compound will be the ones to cause the oxidation, there will be less decomposition of the regenerated color by those rays which are not absorbed by it. In a general way we should therefore expect what Herschel found, "that the restoration of the colour was operated by rays complementary to those which destroy it in the natural state of the paper."

In the case of the poppy extract there is nothing to show what reaction takes place on adding alcohol. This is immaterial to a certain extent. Everything becomes intelligible provided the colorless substance due to the addition of alcohol is oxidized by light and air. Addition of acid will then restore the original color only in the shaded portions where no reaction has taken place.

Herschel[1] points out "that the rays effective in destroying a given tint, are in a great many cases, those whose union produces a colour complementary to the tint destroyed, or at least one belonging to that class of colours to which such complementary tint is to be referred." He admits, however, that this rule is not general and that it "is to be interpreted with considerable latitude." The whole trouble is in the wording of the rule. The first law of photochemistry is that only those rays can act chemically which are absorbed. It is not true that all the rays, which are absorbed, act chemically as regards any particular reaction. It is consequently not true that all rays act which are complementary to the color of the reacting substances. In addition to this, there is also a difficulty in determining what constitutes a complementary color unless one makes a spectroscopic examination. The unaided eye often fails to recognize all the colors reflected from any given object. An admirable instance of this is cited by Herschel[2] himself in regard to the red in grass and leaves.

201. The ruddy tint which comes out when the green is destroyed by light, is in all probability that which gives the whole colour to sere and withered leaves, whether simply disclosed by the destruction of the green which masked it in the live state of the leaf, or matured by exposure to light during the whole season, either out of the elements of the green colouring matter destroyed, or from the other juices of the vegetable. It deserves to be noticed in connection

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[1] Phil. Trans., 132, 189 (1842).

[2] Ibid., 132, 200 (1842).

with this, that all the lively vegetable greens have a large portion of red in their composition, and are in fact dichromatic. A good example of such a colour is a solution of sap-green, which, used as a prism, is seen to transmit both red and green rays, separating them by a broad interval which increases as the thickness or density of the solution is increased, the red ultimately preponderating, and the green being extinguished. If we view a garden or shubbery through a glass of a pure, and deep red colour, every shrub, such as the laurel, of a lively and brilliant foliage, and especially green grass, will appear scarlet. Under such circumstances, a grass-plot, seen in contrast with a graveled walk, shows as light on darkness, contrary to their habitual order of illumination. So great is the quantity of extreme red light reflected by a green sward, as actually to appear bright in opposition to clear blue sky seen through the same glass in the quarter of the heavens opposed to the sun, and that at noonday. The aspect of nature, indeed, when viewed through coloured glasses, is fraught with curious and interesting matter of optical remark; but to give them their full effect they must not be merely applied to one eye for a few moments, as in the case of Claude Lorraine glasses. They should be worn as spectacles, both eyes being used, all lateral light carefully excluded by black velvet fringes, and their use continued till the pupil is fully dilated and the eye familiarized with the intensity and tone of the illumination. So used, not only are the ordinary relations of all lights and colours strangely and amusingly deranged, but contrasts arise between colours naturally the most resembling, and resemblances between those naturally the most opposed. We became aware of elements in the composition of tints we should otherwise never have suspected, and the singularities of idio-chromatic vision which seem so puzzling, when related, cease to be matter of any surprise.[1]

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[1] The late celebrated optician, Mr. Troughton, who was a remarkable instance of this sort of vision, informed me that he could not distinguish the scarlet coats of a regiment of soldiers from the green turf on which they were

The strict applicability of the law in regard to the relation between chemical action and the absorption of light has been shown by Timiriazeff[1] for chlorophyll in the Croonian lecture before the Royal Society.

"When I first set to work, the current idea was that the photochemical process going on in the green leaf under the influence of light ought to be considered a function of its luminosity. This belief was chiefly based on J. W. Draper's classical experiments on the spectrum. From a theoretical point of view it seemed to me highly improbable that a chemical process so essentially endothermic, and consequently depending on energy of radiation, should stand in a direct relation to a purely physiological property of radiation, having no existence outside the organ of sight. Light, taken in the narrow sense of the word, does not exist for the vegetable world, but facts brought forward by such an authority as Draper were not to be so easily dismissed on the single ground of their improbability. However, a careful study of Melloni's classical memoir on the shifting of maximum heat with the state of purity of the spectrum brought me on the track of a considerable experimental flaw in Draper's researches. His spectrum was highly impure; in fact it was obtained by means of a circular aperture three-quarters of an inch in diameter—Wollaston's narrow slit not seeming to be in general use at the time. A sufficient explanation was thus obtained for the coincidence of the chemical effect with the maximum luminosity in the yellow and green rays, this part of the spectrum being practically white, slightly tinged with these colours, and consequently acting by the sum of nearly all the rays of the spectrum, its limits only remaining monochromatic.

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drawn up nor ripe cherries from the leaves of a tree which bore them. His eyes, however, were perfectly sensible to rays of every refrangibility *as light*, but the spectrum afforded him only the sensations of two *colours*, which he termed blue and yellow; pure red and pure yellow rays exciting in his mind the same sensation.

[1] Proc. Soc., 72, 425 (1903).

"The next step was to prove that this coincidence of the two maxima, of luminosity and of the chemical effect, did not in reality exist. A simple inspection of these three curves (the curve of assimilation, that of luminosity and the energy curve), taken from my first (and last) German paper, proves with sufficient evidence that a coincidence of the chemical effect with Fraunhofer's luminosity curve was out of the question, but so far as the visible spectrum is concerned, there exists a decided relation with the energy curve.

"In this first and preliminary research the more simple and convenient method of coloured liquid screens, introduced by Senebier and applied in a more exact form by Daubeny, was adopted. I merely introduced a more correct form of calculation and graphical representation of the results obtained. At the same time I applied the method of gas analysis now in general use, though quite erroneously attributed to Professor Pfeffer.

"But if these results were sufficient to dispose of the current ideas on the importance of the luminosity, based as they were on Draper's experiments, they were not sufficient for the building of another theory. It was impossible, for instance, to consider the decomposition of the carbon dioxide as simply an effect of the relative energy of the radiation. The maximum of energy in a prismatic spectrum lies in the infra-red, and a remarkable experiment of Cailletet (curiously too often omitted in most of the historical sketches of the subject) gave an unequivocal proof that the rays of light, filtered through Tyndall's solution of iodine in carbon bisulphide, were incapable of producing the reduction of the carbon dioxide in a green leaf.

"It was evident that some other principle had to be brought forward in order to explain the absence of any chemical action in the invisible part of the spectrum, as well as its distribution in the visible. The principle that was appealed to was Sir John Herschel's law: that a photochemical reaction may be induced by those rays only that are absorbed by the substance undergoing a change and consequently, as a rule, presenting a complementary colour. It was that, applied to our case, Herschel's law would mean that the reduction of the carbon dioxide must take place at the expense of those rays of the spectrum which are absorbed by the green matter of the leaf—that they must correspond to the absorption bands of chlorophyll.

"Lommel is generally credited with having been the first to enunciate the idea that the reduction of the carbon dioxide may be considered as a function of the energy of radiation and of the degree of its absorption by chlorophyll. But this opinion, despite its being very general, is none the less erroneous. Lommel himself admits that the first half of the proposition, concerning the dependence of the energy of radiation, was formulated by me, and I may add that I could not affirm the second half of the truth for the simple reason that it had already been affirmed before me, and consequently before Lommel, by Jamin and Edmond Becquerel. It is only a matter for wonder that, as a physicist, Lommel was not acquainted with Jamin's well-known text-book and the perhaps still better known book of Becquerel "La Lumière, ses Causes et ses Effets."

But of course the main thing was not to express an idea, however exact, but to furnish an experimental proof of its accuracy. *Nullius in verba* is now, as it was centuries ago, the watchword of every man of science. In other words, it was necessary to repeat Draper's celebrated experiment without falling into his error, and there was the chief difficulty. It is generally admitted that this proof was furnished for the first time by my old friend Professor N. Müller, but I am sorry to say that on this point I am again obliged to contradict the general opinion. In fact Müller never furnished the direct proof of this connection between the chemical process and the absorption of light, and he could not do so, because he did not possess the only means of avoiding Draper's error. In his first work, previous to my researches, he experimented in a tolerably pure spectrum, but the light intensity was then insufficient and he could not actually obtain any reduction of the carbon dioxide, but only inferred that it took place, judging by the difference in the intensity of the respiration. In his second paper, which appeared after my publication, he could affirm directly the reduction of carbon dioxide, but only at the cost of the purity of his spectrum. In fact the width of his slit was nearly the same as in Draper's experiment, and the result was practically the same; this time he obtained the maximum effect in the yellow rays.

"If I allow myself to insist on this point somewhat in detail it is not from any vain desire to establish my priority, but because it is my firm conviction that the method adopted by me is now as it was at that time, the only means of avoiding Draper's error. Müller did not devise any means of avoiding and consequently had no chance of escaping it. The dilemma, as fully exemplified by Müller's failure, was the following: if the spectrum is pure the intensity of light is not sufficient to obtain a reduction of carbon dioxide; if, on the contrary, we open the slit in order to increase the intensity of the spectrum, we may be sure beforehand of obtaining the maximum effect in its middle, somewhere in the yellow or green rays. There was but one means of escaping the two horns of the dilemma—it was to increase the intensity by diminishing the dimensions of the spectrum; but then the leaf surfaces being reduced in proportion, the quantities of gas to be analyzed would be too small to be measured in such gasometric apparatus as the chemist of the time (1870) would put at the disposal of the botanist."....

"Armed with the necessary gasometric and spectroscopic methods of research, I could at last repeat Draper's classical experiment without the fear of repeating his error. The result of my experiments was a strict confirmation of Sir John Herschel's law to our case. Not only do the two maxima coincide, but the assimilation curve reproduces very nearly the absorption curve, so far at least as the less refrangible part of the spectrum is concerned. It is to be remarked that the secondary maxima of absorption seem to have no effects but it is subject to doubt, especially after the latest researches of Schunck and Marchlewsky, whether they appertain to the principal chlorophyll constituent or to some products of its decomposition.

"The same results were obtained later by quite another method. The dissociation of carbon dioxide represented by this curve, the 'photolysis' as it may be called, is the first and by far the most important stage of the whole process, being directly dependent on the external source of energy. But it is closely followed by the photosynthesis of organic matter. Though, thanks to the brilliant researches of Horace Brown and Morris, we now know that starch is neither the first nor by far the only product of the carbon dioxide at the short interval of some minutes, and, what is of still greater importance, its presence may be easily shown by the well-known iodine test.

"If the reduction of carbon dioxide be considered a function of those waves of light which correspond to the chlorophyll absorption bands, and, on the other hand, the production of starch is the next stage of the same photochemical process, it may be fairly presumed that this production of starch in a spectrum will be strictly localized, restricted to the absorption bands of chlorophyll. In other words, a spectrum of sufficient intensity, projected on a living leaf previously depleted of its starch, will impress in this leaf an invisible image of the chlorophyll absorption spectrum formed of starch grains. This latent image may be developed by the iodine test.

"These provisions have been fully realized in the following experiments. Healthy leaves attached to the living plant (a hydrangea) but previously deprived of their starch, after an exposure of five to six hours to the influence of a small but very bright and pure spectrum, were treated in the well-known way with an iodine solution. They exhibited a well-defined spectrum of chlorophyll with its principal band between B and C very prominent, and a general falling off toward the blue end. Just as in the case of the reduction curve, no secondary bands could be detected.

"The blue and violet rays produced hardly any effect. This last result may be chiefly attributed to the fact that the disappearance of starch is only the resultant of two conflicting processes, of its production and its dissolution, so that at a certain point when the assimilation is not sufficiently intense, the former may be counter-balanced by the latter, no surplus starch being stored in the chloroplast."

According to J. Joffré[1] "the fastness to light of dyed fabrics, depends not only on the nature but also on the amount of the dyes. This last circumstance must not be overlooked when making comparative experiments on the fastness of dyes to light. It is also necessary to expose the samples to the sun at the same time since not only may the sunlight have a greater or lesser intensity, but the state of the atmosphere may effect the results. If one exposes dyed samples to the sun in flasks, one of which contains calcium chloride or some other drying agent, and the other water, it will be found that the fabric in the moist air will be bleached more rapidly than in the dry air. Moisture is therefore favorable to the action of light. This fact explains the long known phenomena that dyed fabrics bleach more rapidly at the sea-shore than inland."

In Dreaper's book on "The Chemistry and Physics of Dyeing," there is a chapter on "The Action of Light on Dyeing Operations, and Dyed Fabrics." After giving some instances of the action of light on dyes the author proceeds as follows:[2]

"Three theories have been put forward to explain the cause of this action. They are of an indirect nature and may be briefly summarized as follows:

(1) *The Oxygen Theory.*—The dyes under the influence of light interact with oxygen, and form colourless compounds.

"Berthollet in 1792 came to the conclusion that oxygen combined with the colours, and made them pale.

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[1] Vogel: Handbuch der Photographie, 4th Ed., 1, 59 (1890).

[2] Dreaper: The Chemistry of Physics of Dyeing, 288 (1906).

"The colour at the end of the exposure is, from this point of view, proportional to the resistance to this action.

(2) *The Ozone Theory.*—The colours are decomposed or altered by the production of ozone (or hydrogen peroxide) in the fibre, chiefly by evaporation of moisture.

(3) *Reduction Theory.*—The dye is reduced by cotton fibre, or directly by the action of light.

"Experiments conducted in the presence of oxidizing agents have given conflicting results. The presence of sodium hydrosulphite solution also gives varying results.

"Whatever be the cause of the results obtained in the presence of oxidizing or reducing agents, it is important to note that dyed fabrics always show an increased fastness against the action of light *in vacuo.* This effect is very marked.

"Similar experiments with sensitive organic compounds are wanting. They should be of equal interest.

"A typical example of this action may be seen when cotton dyed with diamine sky blue B is placed in long glass tubes which are subsequently exhausted by water suction to a pressure of 10 mm (9 mm of which are due to water vapour), and exposed for fourteen days to bright light. The shade remained absolutely unchanged. A comparison trial, which was exposed to the light side by side with the other one, but under ordinary conditions, had entirely lost its colour. The cotton was quite white.

"The same blue cotton sealed in a tube in an atmosphere of oxygen gas lost its colour even more rapidly than the above comparison sample. On the other hand, the colour remained unaltered in an atmosphere of either hydrogen, carbon dioxide, sulphur dioxide, or coal gas. When exposed in nitrous oxide gas the effect produced was very similar to that noticed in the case of oxygen.

"It is evident, therefore, that dyed samples in the absence of oxygen will not fade.

"Berthollet in 1792 noticed that the fading action of colours seemed to be intensified in the presence of an alkali.

In the same way an acid condition seems to retard the fading action.

"The fact that the fading is intimately connected with the presence of oxygen may, therefore, be taken as established. It remains to trace the actual action which takes place. It has been noticed that the evaporation of water at ordinary temperatures leads to the formation of ozone in very small quantities.

"The fading of the colours may, therefore, be due to the direct interaction between the ozone, or hydrogen peroxide so formed, from the oxygen in the air, colourless compounds of unknown composition being produced. The action seems also to be proportional to the moisture present at the time of the experiment.

"Under the influence of the light vibrations the oxygen molecule may be more readily split up, and an action of the following order induced:

$$O_2 \rightleftarrows O + O$$

and this may take place more readily when the oxygen is associated with water molecules.

"Whatever the action, the result is clearly seen in the alteration in colour. The most favorable atmosphere for this fading action is a hot, moist, and alkaline one.

"It has also been noticed that the presence of such seemingly inert substances as alcohol and pyridine vapour will greatly influence the rate of fading. It is greatly accelerated in their presence.

"Although our knowledge is incomplete, we may at least assume that the action is a very complicated one, and beyond recording certain facts, we are confined to most indefinite speculations.

"The influence of the fibre is also a factor to be considered. All fibres do not act in the same way. The fastness of the same dye varies on different fibres. Methylene blue on cotton is faster than on wool. Indigo on the other hand gives more fugitive shades on wool than on cotton.

"Colours dyed on cotton, oxycellulose, trinitro cellulose and jute are said to be all equally fast. This might be put forward as an argument that there is no chemical action in dyeing these fibres, the dye being present in all cases in the same state. On silk 84 percent of the colours experimented with showed no difference; 16 percent were said to be slightly faster.

"There are therefore three factors, at least, which may, under these same conditions, influence the rate of fading, *viz.*, the physical condition of the dye in the fibre, that is to say, its state of division; the possibility of some chemical action between the fibre and dye, and the transparency of the fibre substance in its relation to the passage of the light rays.

"The statement that cotton colours are fast in solution, but not on the fibre, is not correct.

"The general conclusion arrived at, therefore, in the present state of our knowledge, is that the action is an oxidizing one and not a reducing one. In the absence of oxygen there is no change in colour, due to the *direct* action of light. The action is also proportional to the moisture present on the fibre. It is clear also that the constitution of a colour determines its stability.

"An advance in our knowledge of this subject was made by Dépierre and Clouet (*J. S. D. and C.* 1885, p. 245), when these authors discovered that the action of light depended upon its nature. It might be expected that the so-called chemical rays would have a greater efficiency in this action in the same way that they have a greater influence in the decomposition of photochemical salts. As a matter of fact, this is not the case. It must, however, be remembered that we have here a distinguishing action in the case of dyes, due to a colour-filtering effect. This natural screen may therefore in its action veil, or modify, the original effects of the light. The most active rays may only have a chance of acting superficially, in some cases at any rate, and therefore have their normal action incidentally modified. Less active rays which are passed on through the superficial screen may actually have a greater cumulative effect.

"Dufton (*J. S. D. and C.*, 1894, p. 92) has shown that in any case the waves which are most readily absorbed are the most active ones; that is to say, the colours complementary to those reflected produce the greatest effect. This seems to be a general law. The absorption of rays, may, as in the cases given at the beginning of this chapter, produce a state of strain in the dye molecule leading to a different state of equilibrium, or formation of fresh compound, and apart from this the formation of active 'oxygen' compounds would seem to bring about the change in the dye which leads to the change in colour. Assuming the quinonoid theory of colour, it would be necessary to allow that the structure of the dye molecule is profoundly modified."

It would not be fair to take this quotation from Dreaper as representing the most advanced scientific knowledge in regard to the effect of light on dyes, but it at least shows the knowledge of the subject which prevails among those interested in dyeing. It is easy to see what an assistance the theory of Grotthuss would be to any one who started in to work out the details of the subject. For the moment, however, all that I wish to do is to call attention to the fact that the dyes are affected chiefly by the rays which they themselves absorb and consequently that they are made active and that oxygen is only a depolarizer. This relation cannot be extended to other reacting gases. Cordier[1] has shown that the reaction between silver and chlorine is accelerated by the rays which are absorbed by chlorine. Schramm and Zakrzewski[2] have shown that the action of bromine on aromatic hydrocarbons is influenced by some of the rays which are absorbed by bromine.

An interesting example of the effect of depolarizers is to be found in a paper by Neuhauss.[3] "The observation,

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[1] Monatsheft, 21, 660 (1900).

[2] Ibid., 8, 299 (1887).

[3] Zeit. Elektrochemie, 8, 132 (1902).

that the bleaching of dyes by light is an oxidation, suggested an experiment which turned out very successfully, of making the mixture of dyes sensitive by adding hydrogen peroxide. Mixtures of dyes which gave clear pictures in sunlight only after one to three hours, showed the same change in about five minutes after being sensitized in gelatine with hydrogen peroxide."

In a second paper I intend to discuss the question of sensitizers and of halogen carriers. After that will come the application of the theory of Grotthuss to cases in which allotropic changes occur under the influence of light.

The general conclusions to be drawn from this first paper are:

(1) Only those rays which are absorbed can produce chemical action (Grotthuss).

(2) The action of a ray of light is analogous to that of a voltaic cell (Grotthuss).

(3) Even with light-sensitive substances, all of the absorbed rays are not necessarily active.

(4) The presence of a depolarizer increases, or makes possible, the action of light.

(5) Whether any given substance is reduced or oxidized by light depends on the depolarizer.

(6) When two substances react under the influence of light, a determination of the active rays will usually show which substance has been made active by light and which is to be looked upon as the depolarizer.

(7) In many cases of oxidation by oxygen gas, the oxygen acts as a depolarizer.

(8) When chlorine reacts with silver, or bromine with toluene, it is the halogen that is made active by light.

(9) Herschel's experiments with blue-print papers have been accounted for.

(10) The theory of Grotthuss accounts for all action of light on salts.

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A NOTE ON THE EXPERIMENT OF THE CRYOPHORUS

BY A. P. SAUNDERS

The familiar experiment of Wollaston's cryophorus rests on the principle of Watt,[1] according to which water distils from a place of higher temperature to one of lower temperature. As ordinarily carried out with an apparatus consisting of two bulbs containing water, one of which stands in a freezing mixture, the other in the air, the water in both bulbs finally freezes; distillation will then cease when the temperature becomes the same in both bulbs.

The following question leads to some rather amusing considerations: What will be the final conditions of equilibrium if ice does not form in the outer bulb, and there results merely a state of supercooling?

The rules that will govern all possibilities for a true equilibrium starting with ice in one bulb, water in the other, are quite simple.

I. No equilibrium is possible with a difference of vapor pressure, for water then passes from one bulb to the other.

II. No equilibrium is possible with a difference of temperature, for heat then passes from one bulb to the other.

Hence since water and ice of the same temperature and under ordinary pressure, have the same vapor pressure only at 0° C, it follows that if ice remains in one bulb, water in the other, the final temperature must be 0°. Or, for all possible cases, either

(*a*) the temperature of both bulbs rises to 0°, or

(*b*) only one phase survives.

Let us assume both bulbs cooled to —10°. Then the following ways in which the apparatus may be arranged will include all that offer any interest, and essentially all that are possible:

(1) The whole apparatus is adiabatically enclosed.

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[1] Van Deventer: Physical Chemistry, Chap. IV.

(2) The ice bulb (A) is maintained at a fixed temperature below 0°, the water bulb (B) is adiabatically enclosed.

(3) The water bulb is maintained at a fixed temperature below 0°, the ice bulb is adiabatically enclosed.

(4) Both bulbs are maintained at fixed temperatures.

(1) Under arrangement (1) we have ice in A, water in B, both at —10°. By rule I, equilibrium is impossible under these conditions. Distillation takes place from B to A. This causes a difference of temperature and brings rule II into operation. Hence there will be a continuous transference of vapor from B to A, and of heat from A to B. But since the vaporization in B absorbs only the latent heat of vaporization, whereas the condensation in A liberates both latent heat of vaporization and latent heat of fusion, there will be a continuous gain in free heat, and consequently a rise of temperature in both bulbs. The distillation will cease when both water and ice have risen to 0°. Thus the end state will be: water at 0° in B; ice at 0° in A.

If the quantity of water in B was originally small, it may all distil over before this end state has been reached, in which case only the ice phase survives, and its final temperature may be anywhere between —10° and 0°.

In case (1) then, the process goes on as if the two phases were mixed after the supercooling had been brought about. In other words it is a relieving of the state of supercooling without contact between the solid and liquid phases; and further it is an autodistillation process from the point of view of the water, since the heat required for vaporization comes from the condensation of the vapor already formed; or in other words, the warmer ice is heated at the expense of the colder water—the heat being transferred as latent heat of vaporization—and free heat then passes back from the ice to the water; and finally, distillation here goes on from a place of lower temperature to one of higher temperature.

(2) If the ice bulb is maintained at a fixed temperature, say —10°, and the water bulb adiabatically enclosed, the water in B will immediately fall below —10° on account of distilla-

tion, and we shall have the same state of affairs as in (1)—vapor passing from B to A, heat passing from A to B. The temperature of B can never rise to that of A because any approach to that point causes the distillation process to go on more rapidly but the transfer of heat from A to take place more slowly. Conversely, the temperature of the water can never fall to the point where its vapor pressure is equal to that of the ice, for any fall of temperature causes a decrease in the distillation from B to A and an increase in the heat transfer from A to B.

Since no change of temperature is possible in A, the liquid must eventually all distil over from B, and in the end state will be found as ice in A, at the temperature of the bath. This end state is independent of the original quantities of water in the two bulbs.

(3) If B is maintained at —10°, A being adiabatically enclosed, the process will go on again as described under (2), but the variation of temperature will now take place in the ice bulb. The initial temperatures being the same, distillation will be immediately set up from the water to the ice, and this will cause a rise of temperature in the ice. This rise can never bring the ice up to the point where its vapor pressure is equal to that of the water in B because of the continual loss of heat from A to B. Hence all the water will distil from B to A, and in the final state there will only be ice in A at the temperature of the bath about B.

These two cases are on the whole almost identical with the first.

(4) If both bulbs are maintained at fixed temperatures, then whether these be the same or different, the water will finally all be found in that bulb where the vapor pressure is lowest, and in the phase that was originally there.

In the special case where the bulbs are maintained at temperatures such that their vapor pressures are exactly equal, no change will take place, if we assume the baths to be ideally efficient, and indefinitely renewed. But there will be no true equilibrium here, for heat will always pass from the warmer to the colder bulb, and there be taken care of by the bath.

Thus the resulting end states are all such as we should obtain if the two phases were placed in contact, though most of the above arrangements would then be experimentally impossible.

Clinton, N. Y.,
January, 1908.

EQUILIBRIUM IN THE SYSTEM: SILVER NITRATE AND PYRIDINE

BY LOUIS KAHLENBERG AND ROBERT K. BREWER

The fact that silver nitrate is soluble in pyridine has been known for some time. In 1886 Jörgensen[1] prepared the two compounds $AgNO_3.3C_5H_5N$ and $AgNO_3.2C_5H_5N$ and tested their stability under the influence of heat. He also investigated the changes which these salts suffered when exposed to the air, and determined their solubility in different solvents. The molecular weight of silver nitrate in pyridine solution was investigated by means of the boiling-point method by Schmujlow,[2] the electrical conductivity of such solutions was determined by Lincoln,[3] and the difference of potential between such solutions and silver electrodes were measured by Kahlenberg.[4] Aside from the work mentioned combinations of silver nitrate and pyridine have received no further attention.

It is the purpose of the present paper to present the results of investigations which have been made to determine the entire equilibrium curve in the system of silver nitrate and pyridine.

The pyridine was obtained from Merck and was dried over fused caustic potash until the sharpest edges of the latter were no longer affected. The product was then subjected to fractional distillation and the portion passing over between 115° and 116° C at 742 mm pressure was used in the future experiments. The silver nitrate was a very pure product. It was carefully fused in the dark to remove moisture. The salt was then finely pulverized. The saturated solutions of silver nitrate in pyridine were prepared in an apparatus similar to that used by Meyerhoffer and Saunders,[5]

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[1] J. prakt. Chem., 33, 501 (1886).

[2] Zeit. anorg. Chem., 15, 23 (1897).

[3] Jour. Phys. Chem., 3, 469 (1899).

[4] Ibid., 3, 386 (1899).

[5] Zeit phys. Chem., 28, 464 (1899).

the glass screw stirrer being placed in a large hard glass test tube which was in turn immersed in a constant temperature bath. The temperature of the latter was carefully regulated. Below 0° C and down to the freezing-point of the saturated solution ice and salt, and finally solid carbon dioxide, were employed. Above 0°, up to 60° C, a water bath was used, and from 60° to 110° a bath of molten paraffine served the purpose. Temperatures above 0° were read on a thermometer graduated to tenths of a degree, while those below 0° were read on a toluene thermometer graduated to one degree; which permitted estimations to tenths of a degree. These instruments were carefully calibrated by comparison with standard thermometers. Both the bath and the solution were constantly stirred by means of an efficient water motor. The mode of experimentation was simple in character. At intervals of 10° C or less the solvent was stirred with an excess of silver nitrate at constant temperature until equilibrium was secured. This required from one to three hours, the fact that the solution had become constant in composition being determined by analysis from time to time. In all cases samples of the solutions to be analyzed were taken by means of a pipette, the mouth of which was provided with a muslin cap which served as an efficient filter to hold back solid particles. These samples were run into a weighing bottle which was then securely stoppered and weighed. Each sample was then treated with dilute nitric acid in slight excess and the silver content determined by titration according to Volhard with a standard ammonium sulphocyanate solution using ferric alum as indicator. By separate experiment, it was established that the pyridine nitrate in these solutions in no way interfered with the estimation. When solutions of silver nitrate in pyridine are exposed for a long time to the light, they gradually darken. However, repeated determinations have shown that the amount of decomposition is too slight to affect the ordinary analytical results.

The experimental results are presented in the following table, which gives the number of grams of silver nitrate soluble in 100 grams of pyridine. Each figure given is the mean of at least two determinations lying well within the limits of experimental error. As it is extremely difficult to keep solutions constant in temperature below 0° C and especially below —20° C, the results obtained at such temperatures are subject to a relatively larger experimental error. This difficulty was offset by making more determinations; and judging from the smoothness of the curve obtained, the figures secured are probably not far from the correct ones.

TABLE

Temperature	Grams $AgNO_3$ in 100 grams C_5H_5N
Equilibrium between unsaturated solution and solid pyridine.	
—48°.5 C (Freezing point of pyridine)	—
—50.5	3.0
—53.0	6.0
—59.0	9.0
Equilibrium between saturated solution and solid $AgNO_3.6C_5H_5N$	
—65.0 (Freezing point of the saturated solution)	—
—51.25	11.1
—44.0	11.7
—40.0	12.2
—35.0	12.6
—30.0	13.9
—25.0	17.6
—24.0 (Transition point.)	—
Equilibrium between saturated solution and solid $AgNO_3.3C_5H_5N$	
—22.0	18.8
—10.0	20.03
0.0	22.34
+10.0	27.21
20.0	33.64
30.0	40.86
40.0	53.52
45.0	62.26
46.0	63.09
47.0	66.35
48.0	70.85
48.5 (Transition point.)	

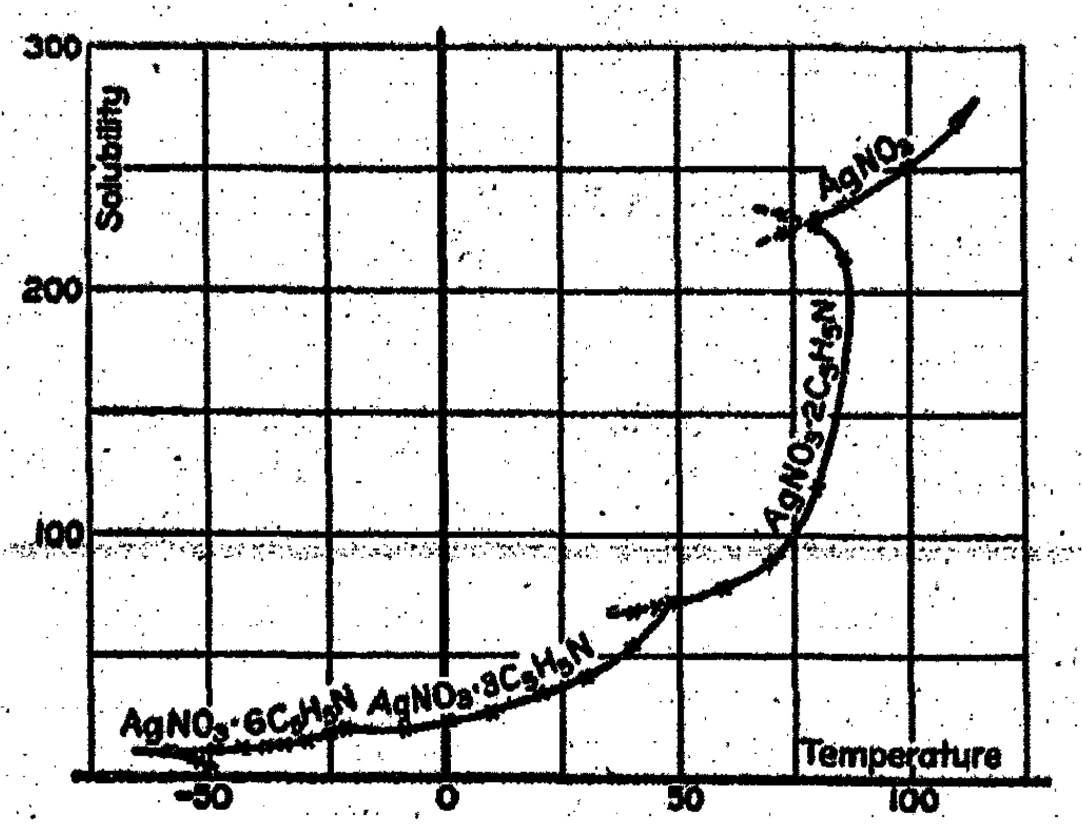
TABLE—(*Continued*).

Equilibrium between saturated solution and solid $AgNO_3 \cdot 2C_5H_5N$

Temperature	Grams $AgNO_3$ in 100 grams C_5H_5N
45.0	69.85
50.0	72.25
60.0	78.60
70.0	89.10
80.0	121.21
87.0 (Indifferent point.)	215.02
80.0	228.5
74.0	230.6
Equilibrium between saturated solution and solid $AgNO_3$.	
74.0	225.4
80.0	230.4
87.0	237.1
90.0	241.9
100.0	253.8
110.0	271.4

The results presented in the table are shown graphically in the accompanying figure, temperature being charted as abscissas and amounts of silver nitrate, in grams, soluble in 100 grams of pyridine, being represented as ordinates.

The freezing point of the pure pyridine was found to be —48.5° C, and the curve between the latter temperature and —65.0° represents the equilibrium between solid pyridine and the unsaturated solution; in other words, this part of the curve is the so-called freezing point curve. At —65° C salt and solid pyridine separate out together and on lowering the temperature further the whole mass congeals. At —65° we have then a quadruple point at which the four phases, solid pyridine, solid salt, saturated solution and vapor are in equilibrium with one another. The solubility gradually increases from —65° to —24° as is shown by the curve. The solid which is in equilibrium with the saturated solution between these temperatures has the composition $AgNO_3.6C_5H_5N$. The crystals of this compound were minute and so unstable above —25° C that an attempt to establish their crystal form was not made. The analysis yielded 25.0 percent $AgNO_3$, whereas the compound $AgNO_3.6C_5H_5N$ would have a content of 26.3 percent $AgNO_3$. The some-



what low result is readily accounted for by the fact that it is practically impossible to free the crystals completely from adhering mother liquor. Hitherto the compound $AgNO_3.6C_5H_5N$ has been unknown.

From —24° to +48.5° the solubility curve changes its trend. The solid which is in equilibrium with the solution has a composition corresponding to the formula $AgNO_3.3C_5H_5N$. By analysis the crystals were found to contain 41.8 percent $AgNO_3$, whereas the formula $AgNO_3.3C_5H_5N$ requires 41.6 percent $AgNO_3$. At 24° we have therefore another quadruple point at which there is equilibrium between the phases, vapor, saturated solution, and the two solids $AgNO_3.6C_5H_5N$ and $AgNO_3.3C_5H_5N$. The latter compound may readily be obtained in form of large, apparently rhombohedral crystals which may be freed from mother liquor by quickly pressing them repeatedly between filter paper.

From 48.5° upward the solubility increases rapidly with the temperature until 87° is reached, at which point the solid in equilibrium with the saturated solution melts and the whole mass assumes a spongy consistency. Further addition of silver nitrate causes a lowering of the temperature of equilibrium until 79° C is reached. From 48.5° up to 79° the solid in equilibrium with the saturated solution is $AgNO_3.2C_5H_5N$. The crystals, which were obtained in the form of long needles, were freed from adhering mother liquor as much as possible and were found to contain 50.8 percent $AgNO_3$, whereas the formula $AgNO_3.2C_5H_5N$ requires 51.87 percent $AgNO_3$. The somewhat low result obtained is easily explained by the fact that it is well nigh impossible to remove the syrupy mother liquor completely from the crystals. At 48.5° then we have another quadruple point at which the phases, vapor, saturated solution and the solids $AgNO_3.3C_5H_5N$ and $AgNO_3.2C_5H_5N$ are in equilibrium with one another.

When the temperature is raised above 79°, after having thus passed the melting-point of the compound $AgNO_3.2C_5H_5N$ as described, the solid phase in equilibrium with the saturated solution again changes, in this case to $AgNO_3$. Thus 79° is another transition point. The portion of the curve from 79° upward was followed to 110°, above which point the vapor pressure of the pyridine becomes so great as to prevent sufficiently accurate determinations under ordinary pressures.

Some of the solid phases changed from one composition to another sufficiently slowly to make it possible to prolong a number of the curves into meta-stable regions. Thus upon cooling the solution in equilibrium with $AgNO_3.2C_5H_5N$ below the transition point 48.5° a smooth curve was obtained to 45°, *i. e.*, 3.5° below the transition point. Below 45° the solid soon changed over to $AgNO_3.3C_5H_5N$, showing that a state of meta-stable equilibrium had been entered after cooling below the transition point. The upper end of this part of the curve could also be prolonged beyond the transition point, 79°, to 74°, thus entering another region of meta-stable equilibrium. Again, on carefully cooling the saturated solution which was in equilibrium with $AgNO_3$ (upper end of the entire curve) the solubility curve was prolonged downward through the transition point, 79°, to 74°, showing another case of meta-stable equilibrium. At temperatures below the last mentioned, the solution became more and more viscous, showing that the transition point had been passed.

Thus at any temperature between 74° and 87° three different solubilities of silver nitrate in pyridine are possible, depending upon the direction of approach to the given point. The very great increase in the solubility between 60° and 110° as compared with that between —60° and 50° is especially noteworthy, nor ought one to lose sight of the fact that there is a very material disengagement of heat when pyridine and silver nitrate combine with each other.

Summary

It has been shown in this paper that pyridine and silver nitrate form three well defined crystalline compounds with each other. The exact temperature limits within which these compounds can exist in stable equilibrium with the saturated solution have been determined. One of these compounds, namely, $AgNO_3.6C_5H_5N$, has not been isolated hitherto, while $AgNO_3.3C_5H_5N$ and $AgNO_3.2C_5H_5N$ have been known. The latter compound melts without decomposition at 87°, whereas the other two lose pyridine upon heating them in an attempt to melt them under atmospheric pressure. The freezing point of pure pyridine has been found to be —48.5°, and the entire equilibrium curve in the system silver nitrate, pyridine, has been established from the freezing point of pyridine up to 110° C.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, January, 1908.

LATENT HEAT OF VAPORIZATION AND SPECIFIC HEAT OF METHYL SILICATE.

BY LOUIS KAHLENBERG AND ROBERT KOENIG

The methyl silicate was prepared by treating silicon tetrachloride with absolute methyl alcohol. The reaction proceeds according to the following equation:

$$SiCl_4 + 4CH_3OH = (CH_3O)_4Si + 4HCl.$$

This method is that employed by Friedel and Crafts[1] who first prepared this ester in the pure state. In order to get a pure product it is quite essential that the methyl alcohol be pure and perfectly anhydrous. Kahlbaum's best methyl alcohol was dried with anhydrous copper sulphate, then redistilled and treated with a small amount of metallic sodium and finally distilled once more, care being taken to exclude the moisture of the air.

The silicon tetrachloride was prepared by passing dry chlorine over hot granulated silicon. The latter product was obtained from Niagara Falls and contained notable amounts of iron. The silicon was heated in a combustion tube in a furnace to dull redness and chlorine, washed by passing it through a copper sulfate solution and then through concentrated sulphuric acid, was then passed over it. The product was condensed by means of a freezing mixture of ice and salt. The tetrachloride was purified by shaking it with mercury, and after the addition of a little sodium it was rectified. The final product boiled at 57° C under a pressure of 740 mm.

It was thought advisable to seize the opportunity to redetermine the specific heat of silicon tetrachloride and also its latent heat of vaporization.

The specific heat determinations were made by means of the well-known method of Berthelot[2] using a thin-walled

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[1] Liebig's Ann., 136, 203 (1865).

[2] Mécanique Chimique, 1, 275–278.

platinum bottle. The latent heats of vaporization were determined by means of Kahlenberg's method, which has been described in detail in this Journal.[1] A platinum condenser, however, was used in this case instead of one of glass.

The specific heat of silicon tetrachloride was found to be 0.1904 between 20° and 40° C. This value is the same as that recorded by Regnault.[2] The latent heat of vaporization was found to be 36.1 which is lower than the value found by Ogier,[3] namely, 37.3.

In the determination a Beckmann's thermometer was employed, which had been carefully corrected by comparison with a Standard thermometer from the Physikalisch-Technische Reichsanstalt. As the rise in temperature was commonly two to three degrees, and as it is quite possible to incur an error of 0.005° in the estimation of this rise, the results are reliable only to about one-fourth of a percent.

In preparing the methyl silicate by the method described, the silicon tetrachloride was placed in a flask and the absolute methyl alcohol was then gradually added in molecular proportions by means of a funnel provided with a glass stopcock. Hydrochloric acid was copiouslv evolved, and the flask was then gently heated to expel that gas as far as possible. The product was then subjected to fractional distillation. The fraction passing over between 120° to 123° was redistilled and a final fraction boiling at 121° at 742 mm. was employed in the determinations. The yield of methyl silicate was 94 percent.

The specific heat of the methyl silicate was found to be 0.5011 between 23° and 115° C, which is the average of several closely agreeing estimations.

The latent heat of methyl silicate at its boiling point, 121°, was found to be as follows: Three independent determinations yielded the values 46.45, 46.47 and 46.53, or an average of 46.48. The value may then be placed at 46.5.

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[1] Jour. Phys. Chem., 5, 215 (1901).

[2] Ann. Chim. (3), 9, 322 (1843). Pogg. Ann., 62, 50 (1844).

[3] Ann. Chim. Phys. (5), 20, 53 (1880).

The work done may be summarized by stating that the latent heat of vaporization and the specific heat of silicon tetrachloride have been redetermined and found to be 36.1 and 0.1904 respectively; and the specific heat and latent heat of vaporization of methyl silicate have been determined for the first time and found to be 0.5011 and 46.5 respectively.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, January, 1908.

NEW BOOKS

Experimental and Theoretical Applications of Thermodynamics to Chemistry. *By Walther Nernst. 13 × 21 cm; pp. X + 123. New York: Charles Scribner's Sons, 1907. Price: $1.25 net.*—A course of lectures delivered at Yale University, on the Silliman foundation, in 1906. It consists of a short introduction, on the application of thermodynamics to chemical changes, and a thermodynamic treatment of results obtained, in Nernst's laboratory in recent years, in the experimental study of certain equilibria at high temperatures. The characteristic feature of the treatment is an application of the hypothesis that the temperature derivatives of the change of energy and of the change of free energy in a thermodynamic process vanish together at the absolute zero. Nernst considers that "the large mass of experimental data upon which the theorem has been successfully tested will probably remove any doubt as to whether the formulas developed by its aid have disclosed new laws to us."

J. E. Trevor

Vorträge über die Entwicklungsgeschichte der Chemie, *von Lavoisier bis zur Gegenwart. By A. Ladenburg. Vierte, vermehrte und verbesserte Auflage. 14 × 22 cm; pp. xiv+417. Braunschweig: Friedrich Vieweg und Sohn, 1907. Price: paper, 12 marks; linen, 13.50 marks.*—This compact and readable history of modern chemistry is so well-known that it need not be criticised in detail. To the fourteen lectures of which it originally consisted, a fifteenth was added in the second edition, a sixteenth was written for the English edition (reviewed 7, 472), and now a seventeenth lecture serves to bring the fourth German edition up-to-date.

We note that (Lect. 2) oxygen was first discovered by Scheele (although Priestley published his results earlier); and that (Lect. 13) the conception of molecular asymmetry as an explanation of optical activity was put forward by van't Hoff "and somewhat later by Le Bel," the order in both cases having been the opposite in the previous edition. In the fifth lecture there are considerable changes in the account of the early history of galvanism. In the fourteenth lecture, dealing with the aromatic compounds, the constitutions of picene and pyrene are added and alterations are numerous. In the fifteenth lecture the new work on the atomic weights of tellurium and iodine is included, and the whole account of the law of mass action has been rewritten. Precise dates are frequently substituted for general statements, and the language has been modernized where necessary The whole work has, in fact, undergone a thorough revision.

In the new lecture (Lect. 17) severe compression has been required to bring the latest development of the science within twenty-five pages. Radioactivity, the theories of Werner and Abegg in regard to valence, solid solutions, and the allotropic forms of iron, tin, selenium and phosphorus are all discussed. In organic chemistry room is found for recent stereochemistry, the Grignard reaction, alkaloids, peroxides and per-acid, and Fischer's work on peptones Catalysis and colloids close the chapter. The apportionment of the limited space is on the whole judicious. Perhaps a half page is too much for Schenck's doubtful conclusions in regard to the relations of red and yellow phosphorus.

Alexander Smith

Die Zustandsgleichung der Gase und Flüssigkeiten und die Kontinuitätstheorie. *By J. P. Kuenen. (Die Wissenschaft. Sammlung naturwissenschaftlicher und mathematischer Monographien. Heft 20). 14×22 cm; pp. x+241. Braunschweig: Friedrich Vieweg und Sohn, 1907. Price: paper, 6,50 marks; linen, 7.10 marks.*—This substantial volume is a fairly comprehensive monograph on the theory of fluids, by a competent authority. It is a mine of information about the numerous attempts that have been made to formulate the relation obtaining between the pressure, specific volume, and temperature of one-component fluids. Four chapters are devoted to comparisons with the results of experiment. The text is happily free from complicated developments of molecular-kinetic theory.

J. E. Trevor

Traité de Physique. *By O. D. Chwolson. Ouvrage traduit sur les Éditions russe et allemande par E. Davaux. Édition revue et considerablement augmentée par l'Auteur, suivie de Notes sur la Physique théorique par E. Cosserat et F. Cosserat.*

Tome premier, second fasicule; 16×25 cm; pp. 409–559. Paris: A. Hermann, 1906.

Tome deuxième, second fasicule: 16×25 cm; pp. 203–431. Paris: A. Hermann, 1906.

The issue of the French edition of Chwolson's big treatise on physics continues with the appearance of the second part of each of the first two volumes. These parts are respectively concerned with the gaseous state of bodies, and with refraction, dispersion, and transformation of radiant energy. An illustrated article on aerial navigation is new, not having been included in the Russian original or in the German translation. For details of the plan and character of the work, reference may be made to an earlier notice, 10, 303.

J. E. Trevor

Müller-Pouillets Lehrbuch der Physik und Meteorologie. *Herausgegeben von Leop. Pfaundler. In vier Bänden. Zehnte umgearbeitete und vermehrte Auflage. Zweiter Band, erste Abteilung, drittes Buch: Die Lehre von der strahlenden Energie (Optik); von Otto Lummer. 16×24 cm; pp xxii+880. Braunschweig: Friedrich Vieweg und Sohn, 1907. Price: paper, 15 marks.*—This is the volume on optics of the new edition of the popular Müller-Pouillet handbook of physics. It will be widely recalled that the aim of this work is to give an extensive treatment of physics, from the experimental side and without employment of the higher mathematics. In the revision of the present volume the text has been greatly changed, both in the sequence of topics and by the introduction of new matter. Interesting new features are the complete overhauling of the discussion of spectrum analysis, and the description of the newest Zeiss constructions in the chapter on optical instruments. The big volume is profusely illustrated. Especially notable are plates of emission and of absorption spectra, beautifully printed in colors.

J. E. Trevor

Über die bisherigen Beobachtungen im ultraroten Spektrum. *By Wilhelm Beetz. 15×23 cm; p. 45. Leipzig: Johann Ambrosium Barth, 1907. Price: paper, 1 mark.*—A monograph on the infra-red spectrum. The author discusses methods of dispersion of infra-red light; the effects of it, as determined by thermometer, thermopile, bolometer, radiometer, phosphorescent plates, and photographic plates; dispersion in non-conductors and reflection by metals and emission by various sources. An extensive bibliography is appended.

J. E. Trevor

L' Électricité, considérée comme Forme de l' Energie. *Les Notions fondamentales, le Potentiel et la Quantité d'Electricité. By E. Ariès. 16 × 25 cm; p. 58. Paris: A. Hermann, 1906. Price: paper, 2.50 francs.*—An interesting outline of the theory of electricity, developed in a logical way from the fundamental ideas of electric potential and of quantity of electricity. Well worth examination, even if only as a specimen of applied scientific epistemology.

J. E. Trevor

Quadratic Forms and Their Classification by Means of Invariant Factors. *By T. J. I'A. Bromwich. (Cambridge Tracts in Mathematics and Mathematical Physics, No. 3). 14×22 cm; pp. vi+100. London: Cambridge University Press, 1906. Price: paper, 3s. 6d. net.*—The third of the carefully prepared Cambridge tracts on special topics of mathematics and mathematical physics presents the theory of quadratic forms in a manner planned to give a fairly complete account in minimum space. The method employed lends itself to geometrical explanations, and these are freely given. The chief chapters treat a single quadratic form, a family of these forms, and theorems concerning the invariant factors of such a family. In the closing chapter, the utility of the theory is illustrated by various applications made of it. *J. E. Trevor*

Annuaire pour l' An 1908. *Publié par le Bureau des Longitudes. 10 × 15 cm. Paris: Gauthier-Villars. Price: paper, 1.50 francs.*—The issue for the current year of the official French tabulation of astronomical, physical and chemical data. The special features are several essays on astronomical subjects.

J. E. Trevor

A History of Chemistry. *By Hugo Bauer. Translated by R. V. Stanford. 12 × 19 cm; pp. 232. London: Edward Arnold. New York: Longmans, Green and Co., 1907. Price: $1.00 net.*—The chapters are entitled: the chemistry of the ancients; the period of alchemy; the period of iatrochemistry; the period of phlogistic chemistry; the period of Lavoisier; the period of the development of organic chemistry; the chemistry of the present day.

This is a very readable little sketch. From the biographical notices scattered through the book, one sees that a life in a laboratory is a healthy one. If one is a distinguished chemist, one has an even chance of living to be over seventy. *Wilder D. Bancroft*

Photochemie und Photographie. *By Karl Schaum. (Handbuch der angewandten physikalischen Chemie. Herausgegeben von G. Bredig. Band IX.) I. Teil. 16 × 24 cm; pp. viii + 228. Leipzig: Johann Ambrosius Barth,* *1908. Price: paper, 10 marks.*—The first part is essentially photometric and the actual photochemistry and photography will be in the second part. Radiation and the measurement of radiation form the subject of this volume. The facts are presented well and the book will be very useful though of course not so interesting to chemists as the forthcoming volume on photochemistry proper.

Wilder D. Bancroft

Die elektrochemische und elektrometallurgische Industrie Grossbritanniens. *By John B. C. Kershaw. (Monographien über angewandte Elektrochemie. XXVIII. Band.) Ins Deutsche übertragen von Max Huth. 17 × 24 cm; pp. ix + 180. Halle: Wilhelm Knapp, 1907. Price: paper, 9 marks.*—This is a historical sketch of the development of applied electrochemistry in Great Britain. The subject is taken up under the headings: aluminum; caustic soda and chlorine; calcium carbide; copper; hypochlorite and chlorate; ozone; sodium, potassium and phosphorus; detinning; galvanizing. In an appendix are given eleven important English electrochemical patents.

Wilder D. Bancroft

A COMMENTARY ON THE FIRST LAW OF THERMODYNAMICS

BY J. E. TREVOR

Introduction

Quantitative description of physical and chemical processes non-mechanical in character yet presenting a mechanical side has been greatly extended and generalized by applying to these processes the method employed for the description of purely mechanical changes of state. In mechanics the method consists in measuring a change of the "energy" of a body by the work requisite to alter the level, or the velocity of motion, or the state of strain of the body, and then describing any given mechanical process by formulating the interconversion of the potential and kinetic energies of a body acquiring or losing motion, or by formulating the transfers of mechanical energy that occur between different bodies.

Many processes not purely mechanical in character can be brought into connection with mechanical operations. Processes of this sort are almost coextensive with the range of physics and chemistry. Fusion and evaporation, electric and magnetic attraction, electrolysis, combustion, and radiation, can all be associated with absorption or development of work. The connection may be to some extent indirect, in that the process alters the temperature of an extraneous body or effects some change of state that can be replaced by a change of temperature. If the temperature of a body is raised, the action of the process is that of a development of work expended in overcoming friction; if the temperature of a body is lowered, the action is that of an absorption of work so expended. In any event a change of state of the type in question can be understood to consist of an absorption or development of work, effected either directly, or else through intervention of an operation equivalent to a change of the temperature of another body, or in both of these ways at once.

Changes of state of this type are "thermodynamic" processes. When the "energy" of a body undergoing a thermodynamic change of state is defined to be a quantity whose change of value is equal to the quantity of work directly and indirectly absorbed by the body, and it can be shown that this quantity of work depends only on the end states of the body, a quantitative description of the thermodynamic process is achieved by a formulation of the transfers of energy that occur between the bodies participating in the operation.

The quantity of work directly and indirectly absorbed by a body undergoing a thermodynamic change of state *is* in fact determined by the end states of the body. To exhibit the reasoning by means of which this conclusion is reached, for the class of thermodynamic changes consisting of processes involving compression, expansion, change of temperature, fusion, evaporation, the formation of homogeneous mixtures, and changes of chemical state, is the purpose of the present discussion. The form of the argument is intended to make clear, for a limited class of operations, the actual content of the first law of thermodynamics. Analytical formulations of the law are not considered. They form, properly, a matter for independent examination.

Changes of state of bodies

At the outset it must be clearly understood what is to be meant by certain terms, by a "body," a "change of state," the "path" of a change of state, a "supplementary" change of state, and a "work-development."

Any given material object or assemblage of objects, as long as no portion of it is removed and no extraneous matter is added to it, shall be termed a given "body." A mass of air or of gunpowder, a block of metal, a quantity of brine together with an overlying layer of water vapor, and a closed receptacle together with its contents, are bodies. During the process of heating coexistent brine and vapor contained in a rigid shell, the layer of brine is not a body, for a portion of this object is removed in the evaporation that ensues.

Any body may be brought from any quiescent state to a new quiescent state by effecting a change of its level or its form, by altering its volume or its temperature, by electrifying it or magnetizing it, or by causing it to undergo a chemical change, and the like. When a body has been brought from one quiescent state to another, it shall be said to have undergone a "change of state." And this change shall be considered to be the same change of state, whatever the manner in which the process has occurred. Thus a block of metal may be slowly or rapidly lowered from one position to another, in each case undergoing the same change of state. Again, a given mass of air may be brought from the volume V_1 at the temperature τ_1 to the greater volume V_2 at the higher temperature τ_2, by raising its temperature to τ_2 at constant volume, and then isothermally expanding until the volume becomes V_2; or by isothermally increasing the volume to V_2, and then raising the temperature to τ_2 at constant volume; or by bringing the volume and temperature of the mass to their new values in any relatively abrupt way. In any of these cases the body undergoes the same change of state, namely the change from the state V_1,τ_1 to the state V_2,τ_2. When a change of the state of a body is effected in different ways, it shall be said that the "path" of the change of state is different in the different cases.

By the "state" of a body shall always be understood a quiescent state. The meaning of the term "state" shall not be broadened to include a "steady state," as that of a body rotating about an axis under the action of constant forces, or a "turbulent state," as that of an exploding mass of gunpowder, or as that of a mass of water in which currents are moving and differences of temperature exist.

Supplementary changes of state

It is important to observe that every *actual* change of state is a *spontaneously occurring* change of the state of the assemblage of all the bodies that participate in the process.

Consider an illustration. Under an exhausted receiver, a vertical cylinder contains a block of metal and an overlying mass of air confined by a heavy piston working without friction. When the isolated system under the receiver is in a state of rest, and has in consequence a uniform temperature, the block of metal is instantaneously replaced by another block, of the same dimensions but having a higher temperature. A change of state of the system ensues. The block contracts and its temperature falls; the air expands and its temperature rises; the cylinder and piston become warmer, and the piston moves to a higher level. This actual change of state is a spontaneously occurring change of the state of the system composed of the metal block, the mass of air, and the piston.

As in this illustration, an actual change of the state of an isolated system may involve changes of the states of more than one body. When this is the case, the change of state of each body, or of any group of the bodies, can be *separately* considered. When this is done, it shall be said that the change of the state of each body or group of bodies is *supplemented* by the change of the state of the other bodies of the system. Thus, in the above example, the change of state of the mass of air is supplemented by the change of state of the metal block and the cylinder and piston. Or, again, the change of state of the air and the piston is supplemented by the change of state of the cylinder and the metal block. With reference to any given change of the state of any body or group of bodies, the "supplementary change of state" is the associated change of state of the system composed of all the other bodies in any way participating in the process.

Work-developments

When a change of the state of a body can be described as consisting of the positive or negative action of a force through a distance, the body develops a positive or negative quantity of work, and its change of state shall here be termed a positive or negative "work-development." When the action of a sinking weight or piston is to raise another weight, or to bring a liquid body to a higher temperature by stirring it, or to decrease the volume and increase the temperature of a mass of gas in a cylinder, the change of state of the sinking body is a positive work-development. When the change of state of the lifted weight, of the stirred liquid, and of the compressed gas is supplemented, in each case, by the change of state of the sinking body, these changes of state are negative work-developments. Work-developments, and changes of state that are not associated with supplementary changes, are termed "adiabatic" changes of state.

Classification of thermodynamic changes of state

From this point, the qualification "thermodynamic" shall be understood as applying only to the processes explicitly under consideration, namely those involving compression, expansion, change of temperature, fusion, evaporation, the formation of homogeneous mixtures, and changes of chemical state. Any change of state of this type can be supplemented by a work-development, or else by a change of the temperature of another body, or by both together. This consideration suggests that such changes of state may be conveniently arranged in three classes, according as they are supplemented wholly, or in part, or not at all, by actual positive or negative development of work. Let us consider this classification more closely.

Class 1. Includes every change of state that is supplemented by a work-development.—When a change of the volume and temperature of a mass of fluid contained in a vertical cylinder is supplemented by a fall or a rise of a heavy piston moving without friction, the change of state of the fluid is supplemented by a positive or a negative work-development, for the action of the piston is the action of its weight through the distance traversed by it. When any compression or expansion of a body is supplemented by an adiabatic change of the volume of another body, the change of state of each body is supplemented by a positive or a negative work-development, for the action of either body may be supposed replaced by the action of a constant force or else of a continuously varying force.

Class 2. Includes every change of state that is not supplemented by a work-development, but that is or can be supplemented by a change consisting of a fall of the temperature, or a rise of the temperature, of an extraneous body.—To ensure that the supplementary operation shall consist solely of a change of temperature, let it be supposed that the supplementary body is enclosed in a thermally conducting rigid shell. Changes of state that can be supplemented by a *fall* of temperature are: a rise of the temperature, with a consequent change of the density, of a body enclosed in a rigid shell; the melting of all or a portion of a solid body similarly enclosed; and any formation of a fluid mixture in a rigid shell, or any chemical process occurring in such a shell, when the final temperature of the mass is above the temperature that would be attained if the process were not associated with a supplementary change. Such changes that can be supplemented by a *rise* of temperature are: a fall of the temperature, with a consequent change of the density, of a body enclosed in a rigid shell; the solidification of all or a portion of a liquid body similarly enclosed; and any formation of a fluid mixture in a rigid shell, or any chemical process occurring in such a shell, when the final temperature of the mass is below the temperature that would be attained if the process were not associated with a supplementary change.

Class 3. Includes every change of state that is not supplemented by a work-development, but that is or can be supplemented in part by a work-development supplying the positive or negative work actually absorbed, and in part by a change consisting solely of a fall of the temperature, or a rise of the temperature, of a body.—Such changes are: a non-adiabatic change of the volume and temperature of a fluid; non-adiabatic changes, whether isothermal or not, of the state of aggregation of a body; and any of the changes of state mentioned in the immediately preceding paragraph, when the condition of constant volume of the body is not imposed.

That the proposed classification of changes of state of the type under discussion depends somewhat on the manner in which the changes of state are supplemented is apparent when it is observed, for example, that a change of the temperature of a mass of liquid is a change of the first class when it is supplemented by a development of work expended in stirring the liquid, while it is a change of the second class when it is supplemented by a fall of the temperature of another body, and it is a change of the third class when it is supplemented by a work-development and a fall of temperature acting together.

The work-value of a thermodynamic change of state

Since a change of state supplemented by a *fall* of the temperature of a body can always be supplemented by a mechanical process in which a development of work is expended in overcoming friction; and since a *rise* of the temperature of a body can always be supplemented by such a mechanical process; it is clear that thermodynamic changes of state can always be brought into connection with purely mechanical operations.

Mutually supplementary *mechanical* changes of state of bodies can be expressed in a way such that a quantitative relationship between the changes of state is established. For example, if a body whose weight is w falls from a level h_1 to a level h_0, and this change of state supplements the rise of a body whose weight is W from the level H_0 to the level H_1, the work *developed* by the first body is $(h_1 - h_0)w$, wherefore the work *absorbed* by the body is

$$-(h_1 - h_0)w.$$

And the work *absorbed* by the second body is

$$+(H_1 - H_0)W.$$

Defining the "work-value" of the change of state of either body as the quantity of work *absorbed* by the body during the change, and adding these work-values to obtain the work-value of the change of state of the system of bodies, which work-value is zero, we have

$$-(h_1-h_0)w+(H_1-H_0)W=0,$$

a quantitative relationship between the mutually supplementary changes of state. The possibility of establishing this formulation depends on recognition of the principle that work is neither gained nor lost in any purely mechanical process.

Now, since all thermodynamic changes of state can be brought into connection with purely mechanical operations, may it not be possible, through reference to these operations, to assign to any thermodynamic change of the state of a body a determinate "work-value," in such wise that formulation of the work-value of the change of state of the system composed of all the bodies participating in the process will establish a quantitative relationship between the thermodynamic change and the change of state that supplements it?

In the endeavor to do this let it be determined that when a positive development of work, whether wholly or partly or not at all expended in overcoming friction, can *supplement* a change of the state of a body, the work-value of the change of state shall be the work developed; and that when the development of work can *replace* the change of state of the body—can supplement the supplementary change of state—the work-value of the change shall be the negative of the work developed. In accordance with this determination, to any thermodynamic change of the state of a body shall be assigned a "work-value" defined as follows:

(1) When a change of the state of a body is supplemented by a positive or negative work-development, the work-value of the change of state is the work developed.

(2) When a change of the state of a body is not supplemented by a work-development, but is or can be supplemented by a fall or a rise of the temperature of another body, the work-value of the change of state is

the positive development of work that will replace the fall of temperature, or it is the negative of the positive development of work that will supplement the rise of temperature.

(3) When a change of the state of a body is not supplemented by a work-development, but is or can be supplemented in part by a work-development supplying the positive or negative work actually absorbed, and in part by a fall or a rise of the temperature of another body, the work-value of the change of state is the work that is supplied, plus the positive development of work that will replace the fall of temperature, or minus the positive development of work that will supplement the rise of temperature.

Illustrations of the definition

It will be well to elucidate the above definition, by application to a few illustrative cases.

A mass of liquid ether overlaid by a mass of ether vapor is confined in a vertical cylinder by a weighted piston moving without friction. When the weight on the piston is increased, the center of gravity of the weighted piston sinks through a difference of level $h_1 - h_0$, and the state of the enclosed ether changes to a state of decreased volume, higher temperature, and increased relative mass of the liquid. If the weight of the weighted piston is w, the work-value of the change of state of the piston is

$$-(h_1 - h_0)w;$$

whereupon the work-value of the change of state of the ether is

$$+(h_1 - h_0)w.$$

If the weight on the piston had been *decreased*, the change of the state of the ether would have been a change to a state of increased volume, lower temperature, and decreased relative mass of the liquid; and the work-value of the change would have been negative.

Two masses of air in a horizontal cylinder are separated and maintained at different pressures by a fixed piston. This piston, working without friction, is released, whereupon the masses of air attain equal pressures, and attain temperatures different from their respective initial temperatures. The change of state of the mass of air whose volume is decreased can be supplemented by a mechanical change developing the work U, having the work-value —U. So the work-value of the change of state of the compressed air is +U. The change of state of the mass of air whose volume is increased can be supplemented by a mechanical change absorbing the work U, having the work-value +U. So the work-value of the change of state of this mass of air is —U.

A mass of ice at its melting temperature τ_0 partially fills a rigid shell in thermal contact with another shell containing a block of metal whose temperature is $\tau_1 > \tau_0$. Supplementary changes of state occur, the temperature of the block falling from τ_1 to τ_0,[1] and a portion of the ice becoming liquid water. Since the change of temperature of the block can be replaced by a mechanical change developing a quantity of work U, the work-value of this change of temperature is —U and the work-value of the change of state of the enclosed water is +U.

Again, the change of state of the water is supplemented by an explosion of a mass of gunpowder contained in the adjoining shell. Since the supplementary change of state of the gunpowder can be replaced by the fall of temperature of the metal block previously considered, the work-value of the change of state is again the work, +U, whose development will replace the fall of temperature. And the work-value of the change of state of the gunpowder is —U.

When sulphuric acid and water are mixed, in the absence of a supplementary change the mixture attains a temperature above that of the separate bodies before mixing. When potassium sulphocyanate is similarly dissolved in water, the

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[1] Or, more generally, from τ_1 to $\tau'_1 \geqq \tau_0$, when the operation ceases or is stopped.

resulting solution attains a temperature below that of the separate bodies before mixing. Let these two mixtures be simultaneously formed in two thermally connected rigid shells, the masses of the four component bodies being so chosen that the final temperature of the whole system is the same as the initial temperature—an unessential requirement introduced to simplify the illustration. The change of state of the body composed of the sulphocyanate and water can be supplemented by a fall of the temperature of a block of metal, whose final temperature shall be not below that of the sulphocyanate and water. If the positive development of work that will replace this fall of temperature is U, the work-value of the change of state of the sulphocyanate and water is U. The change of state of the body composed of the acid and water can be supplemented by a rise of the temperature of a block of metal, whose final temperature shall be not above that of the acid and water. If the positive development of work that will supplement this rise of temperature is U, the work-value of the change of state of the acid and water is —U.

In a vertical cylinder, under a piston moving without friction and supporting the pressure of the atmosphere, a mass of air having the temperature τ_1 overlies a block of metal whose temperature is $\tau_2 > \tau_1$. The mass of air undergoes a thermodynamic change of state supplemented by changes of state of the atmosphere, of the piston, and of the metal block. To simplify the matter, let it be supposed that the changes of state of the cylinder and piston consist only of a displacement of the piston.

If the change of volume of the air is ΔV, and that of the metal block is δV, the lower surface of the piston passes through the volume $\Delta V + \delta V$. The change of state of the atmosphere being measured by the work done against the atmospheric pressure p_1 through the volume $\Delta V + \delta V$, the work-value of this change of state is

$$U_1 = p_1(\Delta V + \delta V).$$

The change of state of the piston consists of a transfer to a higher level. If p_2 is the weight of the piston per unit area of its lower surface, the work-value of this change of state is

$$U_2 = p_2(\Delta V + \delta V).$$

The change of state of the metal block consists of a fall of the temperature of the block, and a change δV of its volume under the pressure $p_1 + p_2$. This change of state of the block can be supplemented by a mechanical change developing the work $-(p_1 + p_2)\delta V$, together with a rise of temperature supplementable by a development of work Q. So the work-value of the change of state of the block is

$$U_3 = -(p_1 + p_2)\delta V - Q.$$

The mass of air, now, has increased in volume by ΔV, and has attained a temperature above its initial temperature τ_1. This change of state can be supplemented by a development of work $-(p_1 + p_2)\Delta V$, together with a fall of temperature replaceable by a development of the work Q. So the work-value of the change of state of the mass of air is

$$U_4 = -(p_1 + p_2)\Delta V + Q.$$

The work-value of the change of state of the system composed of all the bodies participating in the thermodynamic process, determined as the algebraic sum of the work-values of the changes of state of these several bodies, is

$$U_1 + U_2 + U_3 + U_4 = +p_1(\Delta V + \delta V) + p_2(\Delta V + \delta V) \\ -(p_1 + p_2)\delta V - Q - (p_1 + p_2)\Delta V + Q = 0.$$

This is correct, for the change of state of the system is associated with no supplementary change of state.

The energy of a body

When it is shown that a change of the state of a body α is or can be immediately supplemented by a mechanical change of the state of a body β_1, which develops a positive or negative quantity of work, together with a fall or rise of the temperature of a body β_2 enclosed in a rigid shell, or by either of these changes of state alone; and the "work-value" of the change of state of α is defined, as above, to be the work developed by β_1, plus the positive development of work that will replace the fall of temperature of β_2, or minus the positive development of work that will supplement the rise of temperature of β_2; the question arises whether the work-value of the change of state of α, so defined, is a *determinate quantity*, whether it has a constant value independent of the change of state actually supplementing the change of state of α, and independent of the path of the change of state of α. When, for example, an isometric[1] explosion of a given mass of gunpowder successively supplements a rise of the temperature of a body β_2 from τ_0 to τ_1, and a rise of the temperature of a body β_2' from τ_0 to τ_2, will the same mechanical process supplement each of these changes of temperature?

When a change of the state of a body can be described as consisting of an immediate absorption or development of work, experiment indicates that the requisite quantity of work is independent of the supplementary operation and of the path of the change of state. Experiment thus indicates that the work-value of the change, as defined, is independent of these circumstances.

Now consider the case in which a change of state A_1 that can be immediately supplemented by a rise of temperature supplements a change of state B_1. The change B_1 can be supplemented by a mechanical change positively developing work. We may now say that any change of state A, or in particular any mechanical change *a* developing work, that will supplement B_1, and any change of state B that will supplement A_1, will supplement each other, irrespective of the path of any of the changes. This statement is very strongly supported by the results of extended experiments made with the calorimeter, an instrument in which changes of state are supplemented by a change of the temperature of a body, and by the results of experiments in

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[1] At constant volume.

which changes of state, especially changes of the temperature of a body, are supplemented by the falling of a weight or by other mechanical operations. Such experiments also indicate that the quantities of work developed in the changes *a* are the same. Denote this quantity of work by W. Now, by the above definition, the work-value of each of the changes of state *a*, and the work-value of each of the changes of state A, each of which can be supplemented by a rise of temperature, is $U_a = -W$. And, by the definition, the work-value of each of the changes of state B, each of which can be immediately supplemented by a fall of temperature, is $U_b = +W$. It is thus shown to be supported by extensive experimental evidence that the work-value of *any* of these changes of state is independent of the supplementary operation and of the path of the change of state. And it is shown that, whenever U_a, U_b are the work-values of mutually supplementary changes of state, the algebraic sum of these work-values is the work-value, zero,

$$U_a + U_b = 0,$$

of the process consisting of the mutually supplementary changes.

Finally, consider the case in which a change of state A_1 that can be immediately supplemented by a positive or negative work-development *together* with a rise of temperature supplements a change of state B_1. The change B_1 can be supplemented by a mechanical change positively or negatively producing work, *together* with a fall of temperature, which fall can in turn be replaced by a mechanical change developing work. We may now say that any change of state A, or in particular any mechanical change *a* positively or negatively developing work, that will supplement B_1, and any change of state B that will supplement A_1, will supplement each other, irrespective of the path of any of the changes. This statement is supported by the results of very extended calorimetric determinations and measurements of work. Such experiments also indicate that the net quantities of work developed in the changes a are the same. Denote this quantity of work by W. Now, by the definition of the work-value of a change of state, the work-value of each of the changes of state a, and the work-value of each of the changes of state A, each of which can be replaced by any of the operations a, is $U_a = -W$. And, by the definition, the work-value of each of the changes of state B, each of which can directly or indirectly be supplemented by any of the operations a, is $U_b = +W$.

It is thus shown to be supported by very extensive experimental evidence that the work-value of any thermodynamic change of the state of a body is independent of the supplementary operation and of the path of the change of state. And it is shown that, whenever U_a, U_b are the work-values of mutually supplementary changes of state, the algebraic sum of these work-values is the work-value, zero,

$$U_a + U_b = 0,$$

of the process consisting of the mutually supplementary changes.

When it is established that the work-value of any thermodynamic change of state is a determinate quantity, it is established that

The work-value of any thermodynamic change of the state of any body is equal to the corresponding change

$$E_2 - E_1$$

of the value of a quantity E, *which quantity is determined by the state of the body, has one value for each state, and contains an arbitrary additive constant.*

The quantity E is termed the "energy" of the body.

The first law of thermodynamics

Let U be the work-value of any thermodynamic change of state. We distinguish three cases, in which the change of state is supplemented wholly or in no part or in part by actual positive or negative development of work.

Case 1.—The change of state is supplemented by a positive or negative development of work U_1, and so can be described as a positive or negative absorption of the work U_1.

Case 2.—The change of state is or can be supplemented by a fall of temperature, replaceable by a positive development of work U_2, or it is or can be supplemented by a rise of temperature, supplementable by a positive development of work U_2.

Case 3.—The change of state is or can be supplemented by a change that is a positive or negative development of work U_1, together with another change consisting of a fall of temperature, replaceable by a positive development of work U_2, or consisting of a rise of temperature, supplementable by a positive development of work U_2.

In the first case, the work-value of the change of state in question is the work immediately absorbed,

$$U = +U_1;$$

in the second case, the work-value of the change is the work absorbed or absorbable through intervention of a change of the temperature of a body,

$$U = \pm U_2;$$

in the third case, the work-value is the work immediately absorbed, plus the work absorbed or absorbable through intervention of a change of the temperature of a body,

$$U = +U_1 \pm U_2.$$

In general, then, the work-value of a thermodynamic change of state is the sum of two terms: the positive or negative work immediately absorbed, and the positive or negative work absorbed or absorbable through intervention of a change of the temperature of a body. These terms are given separate *names*. The positive or negative work immediately absorbed by a body is termed the "work" added to the body, and the positive or negative work absorbed or absorbable by the body through intervention of a change of the temperature of another body is termed the "heat" added to the body.

Accordingly, the work-value of a thermodynamic change of the state of a body is the algebraic sum of the work and heat added to the body during the change; wherefore the sum of the work W and heat Q added to a body in a thermodynamic change of its state is equal to the corresponding change of the energy of the body,

$$E_2 - E_1 = W + Q.$$

Here W, Q are quantities of work whose numerical values are regarded as obtained by experiment.

When the implications of this equation are compared with experience, they are found everywhere to be confirmed in great detail and to the highest attainable exactness. It is thus recognized that the equation formulates a very general natural "law,"—a very general quantitative description of the manner in which thermodynamic processes take place, a very general type of relation between measurable physical quantities.

The statement that the sum of the work and heat added to a body in any thermodynamic change of its state is uniquely determined by the end states of the body is known as the "first law of thermodynamics." The statement that the algebraic sum of the work-values of mutually supplementary changes of state is zero, or in other words that the algebraic sum of the changes of the energies of bodies undergoing mutually supplementary changes of state is zero, is the "law of the conservation of energy," as applied to thermodynamic changes.

Illustrations

Since it is important to understand clearly the meanings of the terms "work," "heat," and "energy," let us consider the employment of these terms in connection with various particular thermodynamic changes of state.

A mass of liquid ether overlaid by a mass of ether vapor is confined in a vertical cylinder by a weighted piston moving without friction. When the weight on the piston is increased, the center of gravity of the weighted piston sinks through a difference of level $h_1 - h_0$, and the state of the enclosed ether changes to a state of decreased volume, higher temperature, and increased relative mass of the liquid. If the weight of the weighted piston is w, the change of the energy of the piston is equal to the work added to it,

$$-(h_1 - h_0)w;$$

and the change of the energy of the ether is equal to the work added to the ether,

$$+(h_1 - h_0)w.$$

Two masses of air in a horizontal cylinder are separated and maintained at different pressures by a fixed piston. This piston, moving without friction, is released, whereupon the masses of air attain equal pressures, and attain temperatures different from their respective initial temperatures. The change of the energy of the mass of air that is compressed is equal to the work W added to it; and the change of the energy of the expanded mass is equal to the work —W added to it.

A mass of ice at its melting temperature τ_0 partially fills a rigid shell in contact with another shell containing a block of metal whose temperature is $\tau_1 > \tau_0$. Supplementary changes of state occur, the temperature of the block falling from τ_1 to $\tau_1' \geqq \tau_0$, when the operation ceases or is stopped. A portion of the ice becomes liquid water. Since the change of temperature of the block can be replaced by a mechanical change developing a quantity of work Q, the change of the energy of the block is equal to the heat —Q added to the block; and the change of the energy of the enclosed water is equal to the heat +Q added to the water.

Again, the change of state of the water is supplemented by an explosion of a mass of gunpowder contained in the adjoining shell. Since the supplementary change of state of the gunpowder can be replaced by the fall of the temperature of the metal block previously considered, the change of the energy of the gunpowder is equal to the heat —Q added to the powder; and the change of the energy of the water is equal to the heat $+Q$ added to the water.

When mixtures, of sulphuric acid and water and of potassium sulphocyanate and water, are formed in two thermally connected rigid shells, the mixtures will attain a common temperature. The change of state of the body composed of the sulphocyanate and water can be supplemented by a fall of the temperature of a block of metal. If a development of the work Q is requisite to replace this fall of temperature, the change of the energy of the sulphocyanate and water is equal to the heat Q added to this body in the original process; and the change of the energy of the body composed of the acid and water is equal to the heat $-Q$ added to this body.

In a vertical cylinder, under a piston moving without friction and supporting the pressure p_1 of the atmosphere, a mass of air having the temperature τ_1 overlies a block of metal whose temperature is $\tau_2 > \tau_1$. The atmosphere, the piston, the metal block, and the enclosed air undergo changes of state.[1] If the change of the volume of the air is ΔV, and that of the metal block is δV, the lower surface of the piston passes through the volume $\Delta V + \delta V$. The change of the energy of the atmosphere is equal to the work

$$p_1(\Delta V + \delta V)$$

added to the atmosphere. If p_2 is the weight of the piston per unit area of its lower surface, the change of the energy of the piston is equal to the work

$$p_2(\Delta V + \delta V)$$

added to the piston. The change δV of the volume of the block, and the fall of its temperature, can be replaced by a mechanical change developing the work $(p_1 + p_2)\delta V$, together with a mechanical change developing a quantity of work Q. So the change of the energy of the block is equal to the work

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[1] As in the previous employment of this illustration, it shall be supposed that the changes of state of the cylinder and piston consist only of a displacement of the piston.

$-(p_1 + p_2)\delta V$ added to it in the original change of state of the system, plus the heat $-Q$ added to it in this change,

$$-(p_1 + p_2)\delta V - Q.$$

The mass of air has increased in volume by ΔV, and has attained an increased temperature. This change of state can be supplemented by a mechanical operation developing the work $-(p_1 + p_2)\Delta V$, together with a change consisting of a fall of the temperature of a body and replaceable by a development of work Q. So the change of the energy of the mass of air is equal to the work $-(p_1 + p_2)\Delta V$ added to the mass, plus the heat Q added to it,

$$-(p_1 + p_2)\Delta V + Q.$$

The change of the energy of the group of four bodies is equal to the sum of the energy changes of the bodies. It is also equal to the sum of the work and heat added to the group in its change of state. Neither work nor heat has been added, so the sum of the energy changes is zero,

$$0 = p_1(\Delta V + \delta V) + p_2(\Delta V + \delta V) \\ - (p_1 + p_2)\delta V - Q - (p_1 + p_2)\Delta V + Q.$$

This equation is satisfied identically.

Heat

It is especially to be noted that positively "adding heat" to a body—"heating" the body—is not in general associated with a rise of the temperature of the body. Nor does a change of the temperature necessarily involve absorption or development of heat. When a mass of air is adiabatically compressed, or when it expands into a vacuum, the temperature of the mass changes, but no heat is added to it. When heat is added to a block of metal, the temperature of the block rises. When heat is added to a mass of liquid water and overlying water vapor supporting a constant pressure, the temperature of the mass is not altered. Heat may be added to a mass of potassium sulphocyanate and water in the process of forming a mixture, and the temperature fall. An addition of heat to a body involves a change of the state of the body, but it may not involve a change of the temperature alone, and it may not involve a change of the temperature at all.

By the positive or negative "quantity of heat" added to a body in a change of its thermodynamic state is *meant* the development of work that will replace the fall, or supplement the rise, of the temperature of another body, which fall or rise, together with a positive or negative or zero work-development, immediately supplements or can supplement the change of state of the body. Stated in a less detailed way, the quantity of "heat" added to a body in a change of its thermodynamic state is the work absorbed or absorbable by the body through direct intervention of a change of the temperature of another body.

This is all that a "quantity of heat" means. To assume it to mean a quantity of an imponderable fluid, or a quantity of the kinetic energy of hypothetical and inaccessible particles, is to replace direct statement of physical facts, made with the aid of clearly defined terms, by a hypothetical interpretation of the facts. And it should not be forgotten that quantities of "work," of "heat," and of "energy," are *auxiliary* quantities, introduced by definition, and employed solely because they are useful in the establishment of *relations between the measurable physical variables* that are concerned in thermodynamic changes of state. It is these *relations* that are sought in the study of thermodynamic changes, and all else is accessory and nothing more.

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THE ELECTROCHEMISTRY OF LIGHT. II

BY WILDER D. BANCROFT

Sensitizers

In the first paper,[1] attention was called to the importance of depolarizers in determining the chemical action of light. In the cases then under discussion, no reference was made to the possibility of the depolarizer changing the sensitiveness of the system in regard to certain rays. Such cases are known and the substances producing such an effect are usually called "optical sensitizers." A more rational distinction would be between depolarizers with marked absorption bands and depolarizers without marked absorption bands.

In 1873 H. W. Vogel was studying the effect of the solar spectrum on silver chloride, bromide and iodide films. In one of his experiments he used an English silver bromide dry plate which had been stained yellow with aniline red to prevent halation. This plate showed a second maximum of sensitiveness in the green. Further investigation showed that this second maximum of sensitiveness corresponded to an absorption band in the spectrum of a solution of aniline red and that the abnormal behavior of the plate disappeared if the dyestuff were extracted with alcohol. This showed a relation between the sensitiveness of a silver bromide plate for certain wave-lengths and the absorption band for one dye. Vogel proceeded to test the matter further.[2]

"I made experiments, now, to see whether other dyes behaved similarly and whether they made silver bromide sensitive for those rays which they absorbed. I first tried coralline. A dilute solution of the same shows in the spectroscope an absorption band, like that of aniline red, between D and E; *it absorbs the yellow and the yellowish-green light.* On the other hand blue passes to a considerable extent. If

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[1] Jour. Phys. Chem., 12, 230–236 (1908).

[2] H. W. Vogel: "Handbuch der Photographie," 4th Ed., 1, 204 (1890).

the sunlight passes through the coralline solution and then through a prism, green and yellow are missing from the resulting spectrum. There is a dark absorption band in the place where yellow and green are usually to be seen.

"I now dissolved coralline in alcohol and added it to my collodion bromide emulsion so that the latter was dyed a deep red. From this collodion, silver bromide dry plates were prepared which were dyed distinctly red. When these were exposed to the spectrum, my prediction was fulfilled. *The plates were sensitive in the indigo, the sensitiveness decreasing in the direction of the clear blue and becoming very slight at F. From there on the sensitiveness increased, becoming nearly as marked in the yellow as it was in the indigo.* A means had thus been found of making silver bromide plates which should be acted on just as readily by the yellow, which had hitherto been considered a chemically inactive color, as by the indigo, which had previously been considered the spectrum color producing the greatest chemical effect.

"From these experiments I was justified in concluding that some other substance would increase the sensitiveness of silver bromide for the red provided that substance absorbed the red to a marked extent. Such a substance I found among the green aniline dyes. It absorbed the red rays pretty thoroughly between the lines D and C; at higher concentrations, the absorption extended beyond D. Yellow, green and blue passed through with practically no absorption. A collodion dyed with this green proved in fact to be sensitive to light down into the red.

"The sensitiveness decreased gradually from the indigo to the yellow and was almost nothing in the orange. From this point the sensitiveness increased, becoming very marked in the red just where the absorption band occurred.

"From these experiments I feel justified in concluding with a good deal of certainty that we are able *to make silver bromide sensitive to any desired color, or to increase its existing sensitiveness for certain colors. It is only necessary to add a substance which will promote the decomposition of silver bromide* *and which absorbs the rays in question, letting the others pass. The aggravating difficulty in regard to the photographic ineffectiveness of certain colors appears to be a thing of the past."* . . .

"This conclusion met with little favor at first. Distinguished investigators, like Schultz-Sellack,[1] Monckhoven, Carey Lea[2] and Abney, tried to show that the author's results were wrong. In the *British Journal of Photography* for 1874, the discovery of the author was jeered at and made fun of.[3] The Berlin Academy of Sciences, however, recognized the importance of these results and made a considerable grant to the author to enable him to carry on his investigations and to procure suitable spectrum apparatus.

"The reason for the protracted opposition to the author's results is partly due to the fact that very few people at that time were clear as to the connection between chemical action and absorption. Even in 1876 Abney assumed that those rays acted the most on a photographic plate which were transmitted the most completely. Also, there was a widespread ignorance in regard to absorption spectra. Then, too, the majority of those, who tried to duplicate the author's results, failed because they dyed the films too heavily and exposed them for much too short a time. Finally the dyes available at that time were so impure that the silver baths or the collodion emulsion, as it was then prepared, soon became spoiled. As far as the introduction of the principle into commercial practice was concerned, the prospect seemed at first absolutely hopeless. The author himself only obtained one good plate to five bad ones.

"The further work of the author brought to light many peculiar phenomena. At first sight, it appears as though one ought to be able to increase the sensitiveness of the photo-

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[1] Ber. chem. ges. Berlin, 7, 386 (1874). As the text shows, there is absolutely no truth in the assumption recently advanced that it was Schultz-Sellack's investigations which caused the author to study the effect of dyes on collodion.

[2] Although Lea fought the author's results obstinately, he is now, curiously enough, spoken of as one who helped develop color-sensitive photography.

[3] Photogr. Mittheilungen, 11, 100.

graphic plate for the absorbed rays indefinitely by increasing the amount of the dye added. *Experiment showed however that, with many dyes, a deepening of the color not only did not increase the color-sensitiveness of the plate but even decreased it.* Very often the best results were obtained with minimum quantities of the dye.[1]

"Through further investigations he established that by no means all dyes make photographic plates sensitive for the absorbed rays. Thus indigo and aniline blue, which absorb yellow light very thoroughly, do not make photographic films sensitive to yellow. On the other hand, cyanine with its yellow-red absorption has a most marked effect in making plates sensitive.[2] Fuchsine, naphthalene red, aldehyde green and methyl violet also proved effective.

Difference between optical and chemical sensitizing

"A remarkable fact noted by the author (H. W. Vogel) in 1876[3] is that the absorbing dyes in question do not act on a silver bromide collodion which has been prepared with an excess of the bromide. If one dips the plates, however, in a very dilute solution of silver nitrate or in a solution of tannin or morphine, the action of the dye becomes clearly marked.

"Naphthalene red is therefore not capable by itself of making a silver bromide collodion sensitive to yellow; another

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[1] This is very marked with naphthalene red. To 40 cc lots of cadmium bromide collodion there were added 14, 7 and 3.5 drops respectively of a saturated naphthalene red solution and photographs of the solar spectrum were taken on plates made from this material. The plates, which were dyed the most strongly, showed themselves surprisingly insensitive both for the blue and also for the less refrangible rays. The sensitiveness increased with decreasing amount of dye, and was the greatest in the plates where there were 3.5 drops to 40 cc of collodion. Decreasing the amount of dye still further did not increase the sensitiveness (Pogg. Ann., 153, 233; also Ber. chem. Ges. Berlin, 7, 275). With fuchsine the effect of dilution is much less marked. Later the author found that one can add the dye to the prepared photographic plate, by pouring a solution of the dye over the plate and allowing the latter to dry (Phot. Mittheil., 12, 286).

[2] Cyanine was first studied by the author in 1875. See Ber. chem. Ges. Berlin, 8, 1635 (1875).

[3] Ber. chem. Ges. Berlin, 9, 667 (1876).

substance is necessary which reacts readily with free iodine or bromine. Cyanine behaves in the same way. One is therefore obliged to distinguish between those substances which make silver bromide sensitive for certain rays of the spectrum on account of their optical absorption bands, and the ordinary sensitizers, which produce their effect by reacting chemically with iodine and bromine.

"These latter sensitize the plate directly, provided they do not weaken the optical absorption of the silver halide while the former act only in presence of a substance which reacts with iodine or bromine.

Optical sensitizers

"The author therefore named the dyes in question *optical sensitizers* to distinguish them from the *chemical* ones. It is quite conceivable that a substance may be both an optical and a chemical sensitizer and a careful study will doubtless bring such substances to light. It is just as conceivable that dyes may not always show the desired action in presence of a chemical sensitizer, especially not if the dye tends to decompose the sensitizer.

"*The action of the dyes is extraordinarily different with different kinds of plates even though the silver halide be the same.* The effect is strongest with *dry silver bromide collodion plates.* All the experiments referred to were made with *dry silver bromide collodion.* Many dyes, such as methyl-violet or cyanine, work admirably with dry silver bromide but have little or no action on wet silver bromide films moistened with silver nitrate solution.

"Entirely different is the action on the modern gelatine plates. In these the silver bromide is quite different in nature and its behavior is correspondingly different. Gelatine itself ranks as a weak chemical sensitizer whose presence is just as necessary for the action of the *optical sensitizer* as is silver nitrate or morphine in the case of the silver bromide which is sensitive to the violet.

"Here also it is surprising that methyl violet and fuchsine have only a very slight effect on a silver bromide gelatine whereas they are very effective in making a silver bromide collodion plate sensitive to the yellow.

"With all these optical sensitizers the effect was in complete harmony with the theory given, that *they made the photographic film, and especially a silver bromide one, sensitive for those rays which they themselves absorbed.* In connection with this, the author noticed that many dyes not only increase the sensitiveness for the rays that they themselves absorb but they also *decrease* the sensitiveness for the more refrangible rays. This is very marked with fuchsine. Here the yellow-sensitiveness of silver bromide colored with it is distinctly greater than the sensitiveness for the blue, which is ordinarily much the greatest. The sensitiveness of the dyed plate to the blue is less than that of the undyed plate.

"With the other dyes the increased sensitiveness for the absorbed rays also goes hand in hand with a decrease in the sensitiveness of the adjacent more refrangible rays.

"Thus silver bromide, dyed with naphthalene red, is much more sensitive to the yellow than the ordinary silver bromide; but it is less sensitive to the blue-green lying next it in the spectrum than is pure silver bromide. A similar result is to be noted with rosaniline picrate and with aldehyde green.[1]

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[1] Ber. chem. Ges. Berlin, 7, 978 (1874). This remarkable phenomenon, as I remarked elsewhere in 1874, runs parallel with the anomalous dispersion, described by Kundt (Pogg. Ann., 142, 163; 143, 259; 114, 128) which actually occurs in the solutions of the dyes used by me, the index of refraction of the absorption band being increased a good deal on the side toward the red and decreased on the other side.

The increase in the refractive index corresponds to an increase in the sensitiveness and the decrease of the same to a decrease in the sensitiveness, so that the chemical action of light appears to be dependent on the velocity of light in the exciting medium. I [Vogel] cite this passage because of its bearing on similar theories advanced ten years later by Dr. E. Albert (Photo. Corresp., 1884, 133).

Another peculiarity, mentioned by me in 1874, in regard to the partial increased sensitiveness to special colors, due to substances with absorption bands, is that the maximum of the photographic sensitiveness caused by an optical sensitizer does not coincide exactly with the absorption band but is

"Further investigations by the author [H. W. Vogel] established the fact that all three silver halides were themselves slightly sensitive to the less refrangible rays. This had not been noticed before because people had exposed the plates much too short a time. With long exposures, however, the sensitiveness of these substances extends down into the red of the solar spectrum, with silver bromide even beyond that and into the invisible infra-red so that the author was able to photograph the infra-red rays.[1]

"Consequently the addition of the dyes really *increases* the color-sensitiveness of the photographic film instead of causing it. How much this increase is appears from an experiment made by the author ten years later, in which a silver bromide plate dyed with eosine showed sixty times the sensitiveness of an ordinary plate towards the yellow rays.

"The author now attempted to dye other films than silver bromide, and obtained a most surprising result with silver chloride collodion dyed with naphthalene red. It showed a sensitiveness which corresponded almost exactly to that of the human eye for blue and red.[2]

"*Further experiments established the surprising fact that*

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displaced somewhat towards the red. Thus naphthalene red absorbs the light between D and E. The absorption begins at E, increases rapidly in the direction of D, reaches a maximum at E ¾ D, and disappears before D is reached. With silver bromide or chloride plates dyed with aniline red, the maximum photographic effect occurs at D or even goes a bit beyond into the orange. With methyl rosaniline picrate, there is an absorption band in the orange between *d* and C. The stronger photographic band due to this is however nearer the red end of the spectrum, close to B.

Even this phenomenon is not surprising since Kundt has shown that the absorption band has no constant position *but is often moved farther toward the red end of the spectrum, the greater the dispersion of the medium* (Pogg Ann. Jubelband, 615). The above-mentioned absorption bands were determined by me for an alcoholic solution while the absorption in the plates takes place in the more refractive collodion layer.

Recently Eder has shown that the high refractive power of silver bromide itself is of fundamental importance and that it has more effect than either collodion or gelatine in displacing the absorption bands.

[1] Ber. chem. Ges. Berlin, 8, 1635 (1875).

[2] Pogg. Ann., 153, 235.

many dyes, which worked admirably with silver bromide collodion, did not produce the same effect on silver chloride collodion.

"This is true for fuchsine, for instance. It makes silver bromide very sensitive to yellow, and affects silver chloride much less. Naphthalene red acts equally well with both salts. These dyes act also upon silver iodide but to a very much lesser extent."

A great deal of work has been done by Eder on the sensitizing action of dyes as the following quotations show:[1]

"When studying the phenomena due to the action of the solar spectrum on dyed and undyed silver bromide, and when determining what part the gelatine plays, it is important to obtain an answer to the question whether silver bromide combines with the gelatine and the dyes or not. The same experimental conditions must hold as in the preparation of a light-sensitive silver bromide emulsion.

"If a silver bromide emulsion, prepared in the usual way, is washed and then run through a centrifugal machine while in the liquid state, the silver bromide can be separated from the gelatine."...

"Silver bromide was freed from all soluble products by repeated centrifugal treatment and washing with hot water, and was dried at 140° C—whereby much hygroscopic water was driven off. According to my analysis it still contained organic substances which were determined quantitatively by igniting and then converting the resulting silver into silver bromide by means of bromine. One hundred parts of silver bromide by weight contained 0.45 part of gelatine in one case and 0.52 part in another case.

"From this it appears that silver bromide, when precipitated in presence of gelatine, absorbs this latter to a certain extent and retains it so obstinately that it cannot be removed by washing with hot water and passing through a centrifugal.

"If eosine or cyanine be added to a gelatine emulsion and this latter then washed, it will be found impossible to wash

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[1] Monatsheft, 90, II, 1131 (1884).

out the dye so completely that the plate will not show a sensitiveness to the yellow in the spectrograph. When silver bromide was removed from a silver bromide emulsion containing eosine, by passing three times through a centrifugal and by being washed three times, the gelatine passing through was, at first, colored red; but the last wash-waters were colorless. In spite of this the silver bromide was slightly reddish when larger quantities of the dye had been used. When only a little eosine had been added, the silver bromide was scarcely perceptibly colored; *but in all cases there was found the maximum of sensitiveness near D, which is characteristic of eosine.*

"This proves that the dye adheres firmly to the silver bromide grains, whether it is on the silver bromide itself or on the gelatine occluded in the silver bromide grain.[1] This fact seems to be of importance in any explanation of '*optical sensitizing.*'

Relations between the absorption bands of dyes and the sensitizing action on silver bromide

"H. W. Vogel has pointed out the general relation between the sensitizing action of dyes and their absorption bands. On taking up the study of this subject, I prepared dry dyed gelatine films[2] and compared their absorption with the photograph of the spectrum obtained with silver bromide gelatine plates dyed in the same way. In all the cases studied by me, the position of the absorption band in the dried dyed film corresponded to the maximum sensitivity of the dyed silver bromide, except that this latter lies somewhat nearer the red than the absorption band. This displacement is not however always very important. With the eosine colors the difference between the maximum of the absorption in the

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[1] In the latter case the gelatine would cause the dyestuff to adhere to the silver bromide in a way similar to that in which protein compounds act in the dyeing of cotton.

[2] Solutions of dyes give absorption spectra differing markedly from those of the dry dyes. The best thing would have been to have worked with dyed films of silver bromide. As these would have been difficult to prepare, I contented myself with dyed gelatine films.

gelatine film and the maximum of the sensitivity of the silver bromide in the yellow-green is 16–20$\mu\mu$."...

"*The maximum of the sensitizing action of eosine on silver bromide gelatine lies nearer the red than the maximum of the absorption in the dyed gelatine.*

"The same is true of aniline red, and also of the other dyes.

"Through the dyed gelatine there therefore pass many rays at the less refrangible end of the spectrum, which still act very powerfully on the similarly dyed silver bromide. If one lets the solar spectrum pass first through a dry gelatine film dyed with gelatine, there ought to be no picture of the yellow-green formed on a silver bromide gelatine plate, stained with eosine, if, as some people assumed, the rays absorbed by the film were those which caused the light-sensitiveness in the plate. Under these circumstances, however, I obtained, in addition to the usual picture of the spectrum in the blue, an intense picture in the yellow at D corresponding to the maximum of the optical sensitizing in eosine bromide plates. Right next to this is a minimum (a completely bare place) which corresponds to the maximum of the absorption of the eosine gelatine.

"It is thus proved that the maximum of the sensitizing with dyed silver bromide gelatine plates is not identical with the maximum of the absorption in dyed gelatine but that the dyeing of the silver bromide itself must be taken into account. I have shown experimentally that the silver bromide molecule is actually dyed. To explain the displacement of the maximum of the photographic sensitivity of silver bromide due to the absorption of light, we must fall back on Kundt's law according to which, in most cases, an increase in the refractive index of the medium causes a displacement toward the red of the absorption bands of the adsorbed dyestuff. Dr. E. Albert[1] has called attention to a similar case with dyed collodion emulsion.

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[1] Photogr. Correspondenz., 1884, 137.

"By means of this observation, I believe that we can explain the behavior of silver bromide gelatine which has been exposed wet under a solution of a dye. The solution of the dye works then like a colored screen. For instance, the picture of the spectrum obtained on a silver bromide gelatine plate exposed under an aqueous eosine solution is more like the one obtained when the light first passes through a gelatine film stained with eosine than like the one obtained with an ordinary dry plate stained with eosine. The absorption band of the aqueous eosine solution at E keeps the light from the silver bromide underneath and limits the action of light to the maximum of sensitiveness near D. This maximum is at about the same place whether the silver bromide is wet or dry.

"If one dyes silver bromide gelatine with mixtures of dyes, these often interfere with each other and sometimes the effect of one appears to be neutralized. This is especially apt to happen when the absorption band of the gelatine dyed with one component coincides with the maximum of sensitivity due to the other component.

Relations between abnormal dispersion of the dyes and the sensitizing action on silver bromide

"It has been proved that most of the dyes, which have a sensitizing action on silver bromide, also show the phenomenon of abnormal dispersion. Dr. Albert advanced the hypothesis that the abnormal dispersion stands in causal relation to the sensitizing. 'Silver bromide is affected chiefly by the short wave-lengths (blue and violet). Through anomalous dispersion, rays of short wave-lengths are brought toward the red end of the spectrum (close by the absorption bands) and these rays act powerfully on silver bromide.' According to Albert the displacement of the maximum of the chemical action toward the red end of the spectrum could thus be explained in a very simple way. He offered this only as an assumption without furnishing any experimental data.

"In the normal spectrum we get shorter and shorter wave-lengths as we pass from left to right. In the abnormal spectrum of a concentrated solution of aniline red acting as a prism, the absorption band is at E and on either side of it are the two halves of the normal spectrum transposed. To the right are the rays of longer wave-lengths (red, orange, yellow and green); to the left from the absorption band are the rays of shorter wave-lengths (violet to bluish-green). As a matter of fact, in the abnormal spectrum of fuchsine the rays C to D½ E have exactly the wave-lengths of the rays G–H in the normal spectrum, and these last rays are those which act the most powerfully on silver salts. It is difficult however to see how a dye could produce abnormal dispersion in a normally produced pure solar spectrum. Still other discrepancies are to be discovered on further examination.

"It appears surprising that dyes give a narrow intensive sensitizing band in the yellow, etc., whereas they usually have a long drawn-out band with no definite maximum in the normal blue and violet of the solar spectrum. Briefly, the sensitizing action in the yellow or red must produce a picture like that of the blue part. In silver brom-iodide gelatine or in silver chlor-iodide gelatine, which shows two maxima in the blue end of the normal spectrum, there must also be two maxima in the sensitizing band at the yellow end of the abnormal spectrum. I have never observed this however when the dye only showed one absorption band. Further, if the dye produced a band of rays of short wave-lengths at a certain point in the spectrum, the maximum of sensitivity produced by a given dye must be different with silver bromide gelatine and silver chloride gelatine because silver chloride is decomposed the most at H, silver bromide between G and F. Consequently the maximum of sensitiveness with silver chloride must lie much less toward the red than in the case of silver bromide. Experiments with eosine and cyanine gave negative results. The maximum of the normal spectrum action on dyed silver chloride, bromide, brom-iodide and chlor-iodide gelatine in the blue part of the spectrum varies with the nature of the silver salt; the position of the maximum sensitizing by a dye in the red end of the spectrum is constant.[1]

"Abnormal dispersion is therefore not sufficient to account for the sensitizing action of dyes on silver bromide, etc.

"According to the statement of other investigators there is no connection between the fluorescence of the dyes and their sensitizing action on silver bromide. I can confirm this from my own experience. Some dyes which fluoresce red (naphthalene red), yellow (certain eosine colors), or green (fluoresceine) are sensitizers, while many dyes (cyanine, aniline red) do not fluoresce but do act as sensitizers. In other words there is no regularity in the matter.

Relations between the sensitizing power of substances and their chemical and physical properties

"All dyes do not cause the same relative increase in the light-sensitiveness of the silver halide salts to the less refrangible rays, many having no effect at all.

"I have experimented with over 140 dyes in silver bromide gelatine in two to three different concentrations and with at least three different times of exposure (varying at least 100–300 fold). Only in a small percentage of cases were sensitizing properties found. While the number of sensitizers, discovered by me is considerable, the action of only a few is intense.

"Within very narrow limits, similar chemical constitutions are accompanied by similar absorption spectra and sensitizing power; as for instance with cyanine iodide, chloride, sulphate and nitrate; with the different salts of rosaniline, etc. This is not saying very much however. This property seems to be a more general one of the derivatives of fluoresceine; thus, fluoresceine and benzylfluoresceine (chrysoline), for instance, are sensitizers for the green rays; the bromine, chlorine and iodine derivatives of fluoresceine (the eosines)

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[1] No account is taken of small and irregular fluctuations which I ascribe to the effect of the atmosphere on the quality of the light.

are sensitizers for the yellowish-green to the green rays. On the other hand this regularity is marred by the practically negligible sensitizing action of the nitro derivatives.

"Since fluoresceine is a derivative of phthalic acid, namely resorcinol phthaleine, I tried phenolphthaleine (red with alkalies) and orcinolphthaleine (red) as well as the bromine and nitro substitution products of the latter, without however any remarkable success.

"Rosaniline sensitizes for yellow and orange while rosaniline sulphonic acid (red) does not. On the other hand both benzaldehyde green and the sulphonic acid of benzaldehyde green (acid green) are sensitizers. Trimethyl rosaniline and the trimethyl rosaniline salts (Hofmann's violet, etc.) are sensitizers for the rays from orange to red, while phenyl rosaniline salts and the salts of phenyl rosaniline sulphonic acid (aniline blue) have no sensitizing powers worth mentioning.

"I could not find any regular relations between the chemical constitution and the sensitizing power of dyes.

"Better results are obtained if we compare the position of the maximum of absorption of colored light by the dye and that of the maximum of the sensitizing action on silver bromide gelatine. From the first one can deduce the latter and one can predict whether the dye will sensitize the silver bromide for green, yellow or red. One can examine the absorption spectrum of dyed gelatine films and can allow for the previously mentioned shifting of the sensitizing bands towards the red. This holds for all dyes *which are sensitizers for silver bromide gelatine.*

"This brings us to the question as to what dyes are sensitizers. I know of no certain way of telling other than by trying a photographic experiment. From the mass of data which I have accumulated I should say that dyes, which sensitize silver halide salts, must possess the following properties:

(1) They must dye the silver bromide grains. The dyes which are powerful sensitizers, are all so-called "substantive dyes."

(2) In the dry state—on dyed gelatine or more properly on dyed silver bromide—their spectrum must contain an intense absorption band even for small amounts of the dye, if they are to effect an extensive blackening of the silver bromide. A narrow absorption band produces a narrow sensitizing band.

"I have previously mentioned that neither fluorescence phenomena nor anomalous dispersion is sufficient for the action of the dyestuffs in making silver bromide sensitive to the less refrangible rays.

"Dr. E. Albert has shown the untenability of the assumption that, at the place of the absorption band, the molecules of the dye acquire an intensely rapid vibration which is communicated to the adjacent silver bromide. Apart from the anomalous dispersion, the molecules of the dye do not vibrate where the absorption takes place; but vibrations are destroyed there either with the production of heat or with the decomposition of the dye.

"One might assume a chemical decomposition of the dye, with the decomposition products reducing silver bromide as a secondary reaction.[1] This view has however been shown by Prof. H. W. Vogel[2] not to be universally applicable.

"According to my view there is a mutual re-enforcement of the action of the silver bromide and the dye, quite independent of any light-sensitiveness of the dye alone.

"Silver bromide combines with the dye through molecular attraction[3] and becomes dyed. The absorbed dye

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[1] This view was expressed by Abney and was based on his experiments with cyanine. Cyanine is decomposed by yellow light. If one covers a glass plate with raw collodion dyed with cyanine, exposes this plate to the spectrum, then covers it with a silver bromide collodion and develops *without a further exposure to light*, a picture appears in the region exposed to the yellow light where the cyanine had its absorption band. A direct addition of the dye with subsequent exposure gave the same result (cf. my "Ausführliches Handbuch der Photographie," 2, No. 6, p. 17 (1883).

[2] Photogr. Mittheilungen, 15, 91.

[3] If one assumes that the dyeing of fibres (wool, etc.) is due to the formation of a chemical compound with the dye, the same assumption may be made here; if not, we assume 'molecular attraction.'

would, if alone, absorb strongly the light corresponding to the absorption band and would convert the greater part of it into heat and only a small portion of it into chemical work (oxidation) because most of the sensitizing dyes are fairly fast to light. The first loss of light I propose to call 'photothermal extinction,' and the other loss 'photochemical extinction.'[1] Silver bromide, etc., intimately mixed with or combined with a suitable dye, causes a larger part of the light absorbed by the dye to be converted into chemical work, whereby the silver bromide is drawn into the reaction. The tendency of the dye to oxidize[2] in the light is supported by the property of the silver bromide to give off the deoxidizing [?] bromine under the influence of light.

"If a photochemical reaction takes place in addition to a conversion of light into heat with colored substances having strong selective absorption, rays of the same wave-lengths cause the reaction and the conversion into heat. The position of the absorption band in the dye remains unchanged, since the same rays are changed now more into heat and now more into chemical work. Considered quantitatively the absorption must then change since the 'photochemical' extinction is added to the 'photothermal' extinction as was shown by Bunsen for the mixture of hydrogen and chlorine and by Marchand for ferric chloride and oxalic acid. In all these cases the maximum of the photochemical decomposition in the spectrum occurs chiefly at the place of the absorption band of the colored constituent.

"From these facts I believe that I am justified in formulating the following as a law of photochemical decompositions.

"The photochemical extinction of a mixture is determined in many cases by the photothermal extinction of one component.

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[1] In logical sequence we have also 'photoelectrical extinction' with certain electrical reactions caused by light. The above nomenclature appears to me more generally applicable and more definite than Bunsen's classification into 'optical' and 'chemical' extinction.

[2] Or to take up bromine.

"If the mixture (or compound) of a colored substance having a strong selective absorption with another substance is decomposed by light, the photochemical decomposition is caused chiefly by rays of the wave-lengths which are absorbed by the first substance with photothermal extinction. In consequence, most of the photochemical decomposition in the spectrum is determined by the colored substance. If the substance with the lesser selective absorption is itself distinctly sensitive to light, this decomposition by light will be more or less strongly marked in addition to that caused by the light-absorbing dye.

"By adding dyes to certain silver salts (especially silver bromide and silver chloride), the sensitiveness of these salts for the less refrangible rays can be increased according to Vogel's discovery, so that the mixture is more sensitive for these rays than either of the components alone, the maximum of the action due to the rays being described by the law just formulated."

In a later paper Eder[1] brings out a number of points in regard to sensitizers.

Indifferent dyes

"There are many dyes which have only a weak and some which have no sensitizing action on silver bromide, and yet which have a decided effect on the formation of the photographic image on silver bromide plates. This effect occurs just where silver bromide usually shows its normal light-sensitiveness, in the indigo-blue, violet and ultra-violet.

"Such dyes cause the Fraunhofer lines to appear clearer and more sharply (just as with anisol yellow) and cause the plate in general to remain clear during development. Such dyes are, for instance, Extra-Para-Blue and Pt-Blue from the factory of Meister-Lucius. Both decrease the light-sensitiveness of silver bromide but the favorable photographic effect on the sharpness of the lines extends from the ultra-violet nearly to the green.

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[1] Monatsheft, 92, II, 1359 (1885).

"Many orange-colored and yellow dyes act both as sensitizers, and not as sensitizers. They prevent halation and at the same time cause the clouds to stand out better against the sky when one is taking photographs outdoors. This secondary effect is shown also by eosine, chrysaniline, etc., which are also sensitizers for yellow or green; but I doubt whether the sensitizing action of these dyes has anything to do with the other phenomenon. Probably the dye prevents the lateral dispersion of light[1] inside the film or the too deep penetration of an intense light.

"According to J. M. Messerschmitt[2] quinine sulphate increases the sensitiveness of the plate to white light and to the ultra-violet. Messerschmitt assumes that this phenomenon is connected with the fluorescence of quinine. According to many experiments of my own, quinine has no favorable action, whether the silver bromide gelatine plate be bathed with it before the exposure or whether it be added to the fused emulsion (as J. Plener has also tried without success). In dilute solution, quinine has no effect on the light-sensitiveness; in concentrated solution it actually decreases the light-sensitiveness. Messerschmitt recommends washing the plate with a quinine solution after it has been exposed and before it is developed; but this also proved futile.

On an alleged abnormal action of the photographic sensitizer, chrysaniline

"In a paper entitled 'Spectrophotometric Investigations of Some Photographic Sensitizers,'' Mr. J. R. Messerschmitt[3] describes an alleged abnormal action of chrysaniline on silver bromide gelatine. If one photographs the spectrum on a silver bromide plate dyed with chrysaniline, there is a strong sensitizing action in the green (as far as D) which is in addition

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[1] So-called "molecular dispersion" or "molecular irradiation" (cf. Eder's Handbuch der Photographie, 2, 54, where irradiation and lateral extension of the photographic image are discussed in detail).

[2] Wied. Ann., 25, 671 (1885).

[3] Ibid., 25, 655 (1885).

to the usual spectrum image with silver bromide.[1] If one allows the spectrum to act on an undyed silver bromide plate, then bathes the plate in a chrysaniline solution (1 : 20000), and develops it, the same result is obtained (according to Messerschmitt). 'This is very remarkable,' concludes Messerschmitt, 'since there can be no question of a sensitizing action on an undyed plate.'

"This result is of vital importance to the theory of the sensitizing action of dyes on silver bromide. It shatters the foundations of the existing theories which are based on the changed absorption of light in dyed silver bromide, and according to which the dye must be present during the exposure.

"I therefore repeated Messerschmitt's experiment and always with a negative result.

"In Fig. 1 (solid curve 5)[2] is shown how the solar spectrum acts on silver bromide dyed with chrysaniline *before the exposure*, provided the latent image is developed in the ordinary way. There is a powerful sensitizing in the green (at E) which manifests itself as an intense band superposed on the usual silver bromide image. At the same time the sensitiveness decreases in the violet and ultra-violet.

"If one photographs the spectrum on an undyed silver bromide plate, bathes the plate with chrysaniline solution and develops with an iron oxalate developer, there appears an image of the spectrum entirely normal in type. It differs scarcely at all from the photograph of the solar spectrum on an ordinary silver bromide plate with the ordinary development. One notices only that the image develops more rapidly and that it extends a trifle farther towards the green as well as farther into the ultra-violet. There is absolutely no sign of a good, characteristic sensitizing band.

"The phenomenon is similar (though less marked) to the one obtained by bathing the exposed plate before de-

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[1] Mr. Messerschmitt mentions at the same time my own identical results on the effect of the spectrum on silver bromide dyed with chrysaniline.

[2] [Not reproduced in this article.]

veloping in dilute sodium thiosulphate (1:10000) on silver nitrate. In this way the total sensitiveness of the silver bromide is increased[1] or the rate accelerated at which the image appears in the developer. An actual, sharply characterized, increase in the color sensitiveness does not occur.

"This experiment therefore turns out favorably to the 'principle of absorption' because the dye acts in one way when it is present during the action of light on silver bromide and can absorb light; and in an entirely different way when it is added after the exposure.[2]

On the relation between the absorption of dyes and the photographic sensitizing action. Determination of the wave-lengths for maximum effect

"It is well-known that the 'sensitizing' dyes, which show an absorption band in the spectrum, produce an increase in the light-sensitiveness of silver bromide for wave-lengths corresponding to those of the absorption band. Further it is a fact that there is never an exact coincidence between the absorption band in a dyed gelatine film and the portion of the spectrum for which the color-sensitiveness is increased. This observation was first made by Prof. Vogel. I myself compared the absorption of dyed gelatine films and the maxima of sensitiveness on the corresponding dyed photographic plate, and had in my previous paper taken the difference between the maximum absorption in gelatine and the maximum of sensitiveness in silver bromide as 16–20 millionths of millimeter in wave-length.

"In the 'Spectrophotometric Investigations of Some Photographic Sensitizers' by J. B. Messerschmitt[3] there are many points of contact with my previously published studies on the same subject.

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[1] It must be admitted that this effect is not always marked and with many sorts of silver bromide gelatine it does not occur at all.

[2] I tested other dyes in the same way. When added *after the plate had been exposed,* not one produced any sensitizing effect and therefore I did not continue the experiments.

[3] Wied. Ann., 25, 655 (1885).

"I shall not discuss the numerous, accurate determinations by Messerschmitt of the absorption of light by eosine, cyanosine, methyleosine, fluoresceine, cyanine, chrysaniline, and diazoamido benzene; determinations which are of great value in increasing our knowledge of the absorption spectra of these substances.

"On the other hand it is of interest in regard to my investigations that Mr. Messerschmitt found the difference between the middle of the absorption band for dyed gelatine and the middle of the sensitizing band with silver bromide to be:

With eosine 29 millionths of a millimeter in wave-length.
With cyanosine 15 " " " " "

This agreement with my results is a satisfactory one.

"In spite of this I made a more careful examination of the absorption bands of several dyes in the dissolved and in the solid state (dyed gelatine films) and compared them with the photographic sensitizing bands which they caused with silver bromide gelatine. In doing this I measured the middle of the most intensive absorption bands and the middle of the maximum photographic action in the yellow, orange, or wherever it might be and reduced the positions in the spectrum to wave-lengths expressed in millionths of a millimeter. These measurements are most accurate when the dye has a narrow, intense absorption band when it usually follows that there is a narrow sensitizing band in the photographic image on a dyed silver bromide plate. The results of these determinations are given in the table.[1]

"If the dyes do not show a narrow absorption band and if the absorption spectrum is unilateral, one-half of the spectrum being completely absorbed, it becomes a much more difficult matter to make a relative determination of the positions corresponding to the light absorption of the dye and to its sensitizing action on a silver bromide plate. With increasing intensity (concentration) of the solution of the

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[1] [Omitted in this article.]

dye, the absorption band extends farther, and it is also difficult to determine on the photographic plate the limits of a unilateral equalized sensitizing. I therefore determined approximately the limit of the intense absorption and the limit of the marked sensitizing of the dyed photographic plate, obtaining the figures given in the table.[1]

"The maximum of sensitiveness in a dyed silver bromide gelatine emulsion is therefore always farther towards the red (Diff. = 15–80$\mu\mu$) than the maximum absorption for dyed gelatine films. As cause of the difference one must fall back on the greater density and the higher refractive index of the silver bromide which absorbs the dye. Since I have also proved that *silver bromide itself* takes up the dye, this discrepancy would seem to be accounted for sufficiently.

"In the article to which I have referred several times, Mr. Messerschmitt complains that it has not yet been satisfactorily established that silver bromide, when acting as a dyed medium, does actually produce the displacement of the absorption spectrum of dyed silver bromide.

Absorption spectrum of dyed silver bromide

"The investigation of this is not easy experimentally, because the silver bromide must be produced under the same conditions as those under which it is formed in the photographic plate.[2] One must therefore prepare the silver bromide in presence of gelatine in the form of an emulsion and must free it from gelatine by means of Plener's centrifugal machine. All the work must be done either in total darkness or in ruby light.

"As a dye for the silver bromide, I selected eosine because this substance gives an intense absorption band and a corresponding sensitizing band; and because it would therefore be easy to determine the positions of the maxima.

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[1] [Omitted in this article.]

[2] Silver bromide precipitated from aqueous solutions or containing collodion emulsion, shows quite a different absorption spectrum in the blue. Therefore I did not use it for my experiments because my comparison was to be with a silver bromide gelatine emulsion.

"When silver bromide is dyed with eosine and washed as thoroughly as possible in a centrifugal machine, it is rose-red and is extraordinarily sensitive to light. The red coloring disappears in a few seconds in sunlight and the silver bromide must therefore be kept in absolute darkness.

"The investigation of the absorption spectrum must therefore be made with great quickness and must be repeated with many different samples. The silver bromide was spread in a thin film on a glass plate and brought, wet or dry, before the spectroscope.

"In the absorption spectrum of the silver bromide, stained with eosine and washed in a centrifugal, the absorption band of eosine is distinctly recognizable; but it is displaced further toward the red end of the spectrum than is the case with the pure dye or with a gelatine film colored with it.

"The middle of the absorption band corresponds to a wave-length of 562–564$\mu\mu$, which is just where the middle of the increased sensitiveness comes for the photographic eosine silver bromide plate, namely at 563$\mu\mu$. The optical absorption of the yellow-green rays of the spectrum by eosine silver bromide coincides in position with the maximum of the sensitizing effect.

"The examination of the absorption spectrum of the eosine silver bromide shows one other interesting fact. In the form that silver bromide is contained in a highly sensitive gelatine emulsion, it shows an absorption over the whole solar spectrum, but strongest in the blue part. In presence of eosine silver bromide, the absorption band for eosine is broadened both towards the red and the green, and there is a gradually disappearing absorption extending in both directions.

"This last gives the clue to the puzzle that very often on either side of the point of maximum sensitizing a faint photographic action can be detected for a surprising distance.

Conclusions

"These results and the figures which have been given are of importance for further conclusions. They show the following things:

(1) The absorption spectra of the alcoholic solution of the dye, of the aqueous solution, and of the dry dyed gelatine films do not any of them coincide with the position of the maximum sensitizing effect on dyed silver bromide gelatine. This is a new proof of this generally recognized fact.

(2) The maximum sensitizing effect on dyed silver bromide is farther toward the red end of the spectrum than the maximum absorption of any of the solutions investigated.

(3) The density of silver bromide (6.563) is so high in comparison with that of gelatine (1.326) that one may well consider the higher density of this refracting medium as the cause of this displacement. Although there are very many exceptions to Kundt's law,[1] yet in these special cases there is a great regularity.

(4) The position in the spectrum of the maximum absorption of the dye (in gelatine) and of the maximum sensitizing action on dyed silver bromide differ as a rule pretty regularly by 30$\mu\mu$. In other words, those light rays which produce the greatest photographic decomposition in dyed silver bromide at the place made sensitive by the dye, have as a rule a wave-length shorter [longer] by 30$\mu\mu$ than those which are absorbed by the dyed gelatine (without silver bromide).

(5) The absorption spectrum of silver bromide dyed with eosine and the maximum of the photographic sensitizing action of eosine on silver bromide coincide exactly. In other words, the light rays which are absorbed by silver bromide containing eosine have the same wave-lengths as those for which the dyed silver bromide shows the increased photographic sensitiveness.

(6) Discrepancies between the absorption spectrum of dyed gelatine films and the photographic image of the spectrum upon similarly dyed silver bromide ought not to be considered exceptions to the 'principle of absorption' for the absorption spectrum of one colored medium does not give any certain

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[1] In aqueous alcoholic solutions, and in many other cases as H. W. Vogel has shown.

clue as to the absorption spectrum in another, similarly dyed, medium."[1]

One would have supposed that these experiments of Eder's had settled the question in regard to the identity of the absorption and the sensitizing bands, but this was not the case. Six years later the matter was taken up again by J. J. Acworth[1] who measured the absorption and the sensitiveness on the same plate. The result was precisely that found by Eder, that 'the positions of the maximum sensitiveness and of the maximum absorption do not coincide when determined on the same plate, and that the latter is displaced toward the more refrangible end of the spectrum.' The amount of the displacement varied more in Acworth's results than in those of Eder and consequently Acworth concluded that this displacement was not due to a greater dispersion or density of the silver bromide plate. Acworth believed that the whole difficulty was to be cleared up by the following explanation put forward by Eilhard Wiedemann.[2]

"The appearance of luminescence is a sign that there are very violent vibrations inside a molecule. Such increased vibrations must obviously occur in all cases where there is an absorption of an incident light ray, for the absorption depends on the increase in the amplitude of the vibrations in the molecule at the expense of the incident light ray. The energy present in these vibrations inside the molecule is converted either into radiations or into heat waves. We can consider both processes as a kind of damping. The first factor is the important one in fluorescence and the second one in absorption without emission of light.

"If a is the amplitude of the incident light, α a value corresponding to the absorption coefficient, β a value which is a measure of the damping, then the amplitude in the absorbing particles at the time t after the beginning of the experiment is given by the expression

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[1] Wied. Ann., 42, 371 (1891).

[2] Eder's Jahrbuch, 1890.

$$\delta = C\frac{\alpha a}{\beta}(1 - e^{-\beta t}$$

where C is a constant.

"The greatest amplitude which can possibly occur is

$$D = C\frac{\alpha a}{\beta}.$$

"If a substance is decomposed by incident light, this decomposition takes place when the amplitude δ in the molecule has reached a definite value in consequence of the absorption. If the maximum value of δ, *i. e.*, D, remains below a definite value, no decomposition at all can take place. The value of D depends both on α and on β. If $x = 0$ there is no absorption, the value of D is also zero and there is no chemical action. If β is very large the conversion of the motion inside the molecule is very rapid and there is no decomposition, despite marked absorption.

"Now β is probably largest for the places of strongest absorption and therefore, if we sensitize a plate with a given substance, that incident rays, corresponding to this maximum absorption, may not produce the maximum sensitiveness while neighboring rays in the spectrum may do so."

I do not know how seriously people have taken this explanation of Wiedemann's, but Acworth's measurements have certainly been looked upon by some[1] as disproving Eder's results. This is not surprising. Acworth worked under what seems at first to be ideal conditions. He measured the two phenomena on the same plate under the same circumstances. There is not much reason to question the accuracy of his experiments[2] and consequently the only place for error is in the interpretation of his results. It seems certain however that his conclusions are wrong. Eder's experiments with dyed silver bromide seem to me to be conclusive though

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[1] Ostwald: Lehrbuch allgem. Chemie, 2nd Ed., 2, I, 1060 (1893); Timiriazeff: Proc. Roy. Soc., 72, 443 (1903); Byk: Zeit. phys. Chem., 62, 488 (1908).

[2] The concentrations of the dyes were *not* the same as in Eder's experiments.

Acworth does not mention them. This being the case, it is necessary to point out the error in the interpretation of Acworth's results. The important thing is to recognize that a silver bromide gelatine film is a two-phase system and not a one-phase system. When we measure the absorption of a dyed plate, our results give us the sum of the absorption of the dyed gelatine and of the dyed silver bromide whereas what counts in the photographic sensitizing is chiefly the dyed silver bromide. In Acworth's results the absorption curve for the silver bromide is apparently practically lost under the absorption curve for the gelatine.[1] It is much the same thing that we should get if we determined the absorption spectrum of an emulsion of chloroform and water to which a little iodine had been added.

There are half a dozen pages in Timiriazeff's Croonian Lecture which bear directly on this question of sensitizers and I therefore quote them.[2]

"The fact that the reduction of carbon dioxide as well as the production of starch is due to the rays absorbed by chlorophyll, may be thus considered as fully established in all its details, the more so that an elaborate bolometric study of the chlorophyll spectrum in the infra-red by Donath, has proved that there are no absorption bands in this region. This accounts for the fact established, as we have seen, by Cailletet, that no reduction can be attributed to the rays filtered through Tyndall's iodine solution.

"We have now to consider the second of the two points mentioned above concerning the connection between the photochemical process and the absorption of light. We have seen that Jamin, Edmond Becquerel and, lastly, Lommel, expressed the opinion that Herschel's law might be applied in our case. But it seemed to me that in this reasoning there was a certain logical flaw, a link missing, between the premises and the conclusion deduced. Herschel's law means that the

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[1] Cf. v. Hübl: Photogr. Corresp., 1895, 550; Bothamley: Brit. Jour. Photography, 43, 471 (1896).

[2] Timiriazeff: Proc. Roy. Soc., 72, 438 (1903).

photochemical effect is confined to those rays of light only which are absorbed by the substance undergoing chemical change. Sir John Herschel applied it himself to chlorophyll, showing that this substance underwent a process of bleaching in exactly those rays of the spectrum which correspond to the absorption bands.

"But in the reduction of carbon dioxide we have quite a different case—the substance undergoing decomposition is a colorless gas and light is absorbed by another substance, chlorophyll. It was decidedly impossible to see in this case a direct application of Herschel's law, and that was one reason the more for my not insisting on this point at the beginning of my researches. But the same reason accounts for my being one of the first to acclaim the importance of Professor Vogel's beautiful discovery of *optical* sensitizers.

"This brilliant achievement not only revolutionized the practice of photography but furnished at the same time that missing logical link, the absence of which did not permit of Herschel's law being applied to the case of the green leaf. Vogel's researches on eosine were shortly followed by Edmond Becquerel's experiments on collodion plates sensitized by an admixture of chlorophyll, so that in less than a year after the publication of my first experiments I was able to give them a rational explanation in the light of Vogel's new theory. This idea, that chlorophyll plays in the living organism the part of an optical sensitizer, which I advanced for the first time in 1875, is now generally accepted, but I suppose very few botanists have had an opportunity of seeing the photographic effect of chlorophyll on a sensitized plate. The late Edmond Becquerel in 1877 kindly showed me his beautiful collodion plates, but the collodion process being now somewhat out of fashion, I tried to find a simple way of applying the sensitizing action of chlorophyll to the gelatino-bromide plates now in general use. Alcoholic solutions are not practicable in this case, and I found it very convenient to substitute a potassium or sodium chlorophyllate, which is easily soluble in water.

"Here is a plate (Ilford ordinary), half of which has been immersed in a bath of chlorophyllate of sodium, and then exposed to a spectrum reduced by means of a yellow filter to its least refrangible part. It may be seen that whilst on the ordinary plate the effect stops short of the line D, in the part that has been immersed in the sensitizing bath there is a bright band corresponding exactly to the principal absorption band of chlorophyll between the lines B and C.

"I tried to push the analogy between the effect of chlorophyll in a sensitized plate and in the green leaf a step further, by showing that chlorophyll is an optical sensitizer, not only in Vogel's but in Sir William Abney's acceptance of the word.

"Sir William Abney admits that an optical sensitizer is as a rule a fugitive dye, *i. e.*, one that rapidly fades in the light. Sir John Herschel's classical researches on the bleaching of paper tinged with chlorophyll, prove that chlorophyll belongs to the above class. I have here a chlorophyll print of a fern leaf. The leaf was applied to a plate coated with a film of collodion tinged with chlorophyll. After a short exposure to direct sunlight we observe that the whole ground is bleached, the parts protected by the leaf retaining their original hue. The image is fixed by a short immersion in a bath of copper sulphate. On submitting such chlorophyll collodion plates to different rays of the spectrum, I convinced myself that this bleaching effect is due to the same rays which effect the reduction of carbon dioxide.

"I may perhaps be allowed to dwell a little longer on this important question of chlorophyll playing the part of a sensitizer. The sensitizers are in general divided into two groups —chemical and optical. The former are considered simply absorbents of one or more of the products of the reaction, the latter are at the same time absorbents of radiant energy. An optical sensitizer is supposed to be at the same time a chemical sensitizer, but the reverse of course does not hold good. The existence of chemical sensitizers was admitted long before Vogel's discovery; many instances of their action may be found in Becquerel's well-known book, and in consequence at a very early date. In 1871, in my Russian work 'Spectrum Analysis Applied to Chlorophyll,' I admitted that chlorophyll may be considered a sensitizer in the purely chemical acceptance of the word. I insisted that the reduction of carbon dioxide being essentially a process of dissociation, and the 'rapidity of dissociation depending on the removal of the products of dissociation,' the plant acts as an absorbent, continually disturbing the equilibrium between the carbon dioxide and the products of its dissociation, and finally we must probably admit 'the existence of two modifications of chlorophyll somewhat corresponding to haemo- and oxyhaemoglobin of the blood, the latter being perhaps capable of originating a product analogous to carbonyl haemoglobin.'

"At the time it seemed to me that these two states of oxidation corresponded to the normal green chlorophyll and to Sir George Stokes's modified chlorophyll, my experiments having put it beyond doubt that the latter was the product of oxidation of the former; but later I discovered another reaction of chlorophyll, which I look upon as highly important from the physiological point of view we are now considering. When a moderately concentrated solution of chlorophyll is acted upon by hydrogen in the nascent state, it is transformed into a substance nearly colorless, or of a pale yellow hue, but possessing a beautiful purple color when highly concentrated. This substance can exist only in a total absence of oxygen. On being brought into contact with air it almost immediately recovers its natural green color. The spectrum of this reduction product of chlorophyll (I propose to call it protochlorophyllin, or simply protophyllin) in a diluted state, is characterized by a total absence of bands in the less refrangible part of the spectrum, but when sufficiently concentrated, it shows a very distinct band nearly corresponding to the II band of chlorophyll and another band about the place of the IV, no traces of the principal band I being present. It was the first case of a product of chlorophyll characterized by the total absence of what had been considered the principal characteristic of the chlorophyll spectrum. It is evident that we have here a reduced constituent of chlorophyll, from which chlorophyll is regenerated almost instantaneously on its being brought into contact with the oxygen of the air.

"Having obtained these important reactions of reduction and regeneration of chlorophyll in its solutions, I took all possible pains to find out the existence of this protophyllin in the living plant. The formation of chlorophyll in etiolated seedlings being a process of oxidation (the fact was demonstrated in my laboratory by Dementieff in 1873), it was quite natural to search in etiolated seedlings for this protophyllin so easily convertible into chlorophyll on being oxidized. The facts exposed in the current literature were rather discouraging, the so-called *etiolin* of the German botanists always presenting the characteristic chlorophyll spectrum. My first steps were also unsuccessful. I obtained, it is true, solutions where the second band was rather more pronounced; in some cases it had even the same intensity as the first band, but I looked in vain for solutions in which the first band would be totally absent, until the idea struck me that the precautions generally taken were not sufficient to eliminate completely the influence of light. I enclosed the small pots with the seeds that were intended to germinate (sunflower seeds proved to be best) in tin cases, which in their turn were kept in a cupboard in a photographer's dark room. The solutions were prepared in the same dark room, all the precautions used in orthochromatic photography being taken. The result was that I obtained solutions of protophyllin without the least traces of the chlorophyll spectrum.

"The coloring power of these solutions being very small, they had to be studied in tubes 50 cm long. In general about ten or twenty cotyledons were used for preparing the necessary solution for filling the tube. But it was sufficient to expose a single cotyledon, or even a part of one, for an instant to the light in order to obtain a solution that would present the characteristic chlorophyll bands. These facts suffice to prove that in the living plant there exists a coloring matter with the properties of reduced chlorophyll, almost instantaneously convertible into chlorophyll on being exposed to light.

"Of course it would be of still greater importance to obtain a direct proof of the presence of this reduced constituent of chlorophyll in the green leaf; this fact alone could account for its playing the part of a chemical sensitizer; but the detection of this substance in the green leaf needs present certain difficulties. As I have just insisted, the solutions of protophyllin possess a coloring power greatly inferior to that of chlorophyll, so that their presence may be easily disguised by the latter. Thus assuming that this reduction of chlorophyll actually takes place in a green leaf, it will hardly be manifested by a change of color or of the spectrum, but simply by a diminution in the intensity of the green hue, by a certain bleaching of the green parts exposed to the light. Now this bleaching has in fact been often observed, but was generally attributed to the migration or change of volume of the chloroplasts—a supposition that seems to me highly improbable when applied to the palisade-parenchyma especially when the rays of light do not fall strictly in the direction of the cell axes. I really think that at any rate the greater part of this bleaching may be accounted for by supposing some of the chlorophyllin to be reduced to protophyllin. To sum up, we may thus admit the existence not only of two, as in the blood, but even of three states of oxidation of the green coloring matter. These transformations may be considered a starting point for a theory of chlorophyll as a chemical sensitizer.

"Having enumerated the chief arguments in favor of the admission that chlorophyll may be considered a sensitizer in both acceptances of the word—a chemical and an optical sensitizer, an absorbent of the products of reaction as well as an absorbent of the active rays—I will try to take a step further and show that it may be considered not only one of the innumerable representatives of the group, but a substance quite exceptionally adapted to this function.

"At the very outset of my researches I was impressed with the idea that such an intensely endothermic reaction as the dissociation of carbon dioxide, must needs stand in some relation to the energy of the radiations involved in the process. At the time we had no direct knowledge of the distribution of energy in the spectrum, but I pointed out that researches in the diffraction spectrum might possibly alter the current notions concerning the relative calorific effect of the different radiations, and prove that the greatest energy should be attributed, not to the dark infra-red rays, but to a certain group of rays in the visible spectrum—possibly the same that are absorbed by the green plant, so that the two maxima —of energy and of chlorophyll absorption—may after all coincide.

"My provisions were fully confirmed by the brilliant researches of Mr. Langley and Sir William Abney. I called attention to this foreseen coincidence in a small note in the 'Comptes Rendus' shortly after the appearance of Mr. Langley's classical paper. My statements of these facts being still contested, the correctness of my quotations being even suspected by Professor Engelmann, I feel myself bound to bring forward the original data. In Sir William Abney's paper in the 'Proceedings of the Royal Society' for 1887, it is shown that the maximum of energy corresponds to the wave-length about two-thirds between 600 and 700 millionths of a millimeter, let us say 666 (a figure easily retained in the memory, it being the number of the beast). The maximum of absorption is somewhere about the two-thirds between the lines B and C, between 686 and 656, consequently again about the wave-length 666 millionths of a millimeter. At a later date Mr. Langley furnished data which I have plotted above,[1] and we shall soon have occasion to apply to them. It must be remembered that Mr. Langley's numbers refer to what he calls "high sun." For the mean intensity of the whole day the coincidence would probably be still closer. We may

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[1] [Not reproduced in this article.]

consider the same question from another point of view. I have made a rough attempt to represent the relative amplitudes of the vibrations corresponding to the different rays of the spectrum, and it may be seen that the greatest disturbances correspond to that region of the spectrum where the principal absorption band of chlorophyll, and therefore the maximum chemical effect on the carbon dioxide, are situated.

"But we may perhaps find a still more convincing argument in favor of the supposition that the photochemical effect of a radiation is a function of its energy, in a comparison of chlorophyll with the other sensitizers, and still more in a comparison of the relative effects of yellow and blue light in the experiment just cited.

"There is an important fact, based on the testimony of such able observers as Eder and Vogel, and made especially conspicuous in a very elaborate paper of Mr. Acworth, the fact that the maxima, the maximum of absorption of light by the sensitizer and the maximum of photographic effect on the sensitized plate, do not strictly coincide—the latter, as a rule, being shifted towards the red end of the spectrum. No explanation has been put forth for this fact, nor does Mr. Acworth offer any, holding at the same time that the fact in itself is past any doubt. But so far as chlorophyll is concerned a curious error seems to have crept into Mr. Acworth's statements. He admits that chlorophyll makes no exception to the general rule, *i. e.*, that the maximum of chemical effect does not correspond to the maximum of absorption in the first band but is shifted to the red end of the spectrum—though an attentive glance at the figure relating to chlorophyll will easily convince one that there is something wrong about it. As in the other cases, Mr. Acworth gives the two curves, the absorption curve and the curve of the sensitizing effect on the photographic plate, in order to show the shifting of the latter towards the red end of the spectrum. But in fact his statement (in both text and figure) concerning the absorption spectrum of chlorophyll is inexact. Here are his very words: "Die Absorption dieser Emulsion ist was die Haupt- und weniger brechbare Bänder betrifft, deutlich ausgeprägt. Dieses beginnt etwas vor C, erreicht bei C⅓D ein Maximum; jenseits desselben ist die Absorption nicht hinlänglich scharf zu verfolgen, um sie genau zeichnen zu können."

"Now it is a fact testified by thousands and thousands of observations that the principal chlorophyll band lies between B and C and not between C and D. On the contrary, Acworth's curve representing the sensitizing effect has its maximum between B and C—nearer to C—exactly where innumerable observations unanimously place the principal absorption band of chlorophyll, and in this respect all we know only confirms the exactness of Mr. Acworth's experiment. Beginning with the late Edmond Becquerel's first experiment and ending with my recent photographs, we always see the maximum of the sensitizing effect corresponding to the band between the lines B and C. It follows that Mr. Acworth places the maximum of photographic effect in the right place, but the maximum of absorption in an evidently wrong place, and it is only by means of this evident error that chlorophyll is made to agree with the general rule.

"In reality the two points perfectly coincide, and as a further consequence chlorophyll must be considered an exception to the general rule of the shifting of the maximum of chemical effect towards the red end of the spectrum. Now it seems to me that the exception as well as the rule might find an explanation in the simple admission that the photochemical effect must be attributed not only to the degree of absorption of a certain group of rays of which the band is composed, but at the same time to the energy of the amplitude of the corresponding vibrations. In every absorption band (in the limits of the visible spectrum) the side nearer to the red end will be composed of radiations possessing a greater amount of energy, and as a consequence of the supposition just made, the maximum effect must be shifted that way until we arrive at that part in the red where the maximum of energy and absorption coincide. At this point there will be no reason for any shifting of the photographic maximum, and so we get an explanation of the curious anomaly presented by chlorophyll as a photographic sensitizer.

"Of course the *experimentum crucis* for testing my hypothesis would be, using Sir William Abney's wonderful method of infra-red photography, to see whether in the infra-red part of the spectrum Acworth's rule would be reversed. But this kind of research is quite out of the reach of a botanist."

Timiriazeff looks upon chlorophyll as an exception to what he calls Acworth's rule; but it must now be clear that Eder was right and that the absorption and sensitizing bands are identical for dyed silver bromide.

The experiments of v. Hübl[1] show that the sensitizing action of a dye may be modified very much by the quantity of the dye in the gelatine acting as a screen.

"A photographic plate is only sensitized by a dye if the silver bromide grain is itself colored. This requisite was first formulated by Dr. J. M. Eder[2] and was later proved experimentally by the author[3] for collodion emulsions. In accordance with Vogel's absorption theory, Dr. J. M. Eder formulated the law that only those rays which were absorbed by dyed silver bromide, could be effective photographically and that the absorption spectrum of the dyed silver bromide must coincide with the region of photographic sensitiveness. Experimental investigations along this line often show surprising irregularities. Depending on the method of working and the composition of the photographic film, the sensitizing band is displaced more or less with regard to the absorption band. In many cases the form of the sensitizing band varies.

"A series of experiments by the author on cyanine and eosine have confirmed the accuracy of Eder's views and have shown that the previously mentioned irregularities depend chiefly on an excess of dye left in the plate. When dyeing the liquid emulsion and not less when bathing the dry plate

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[1] Jahrbuch der Photographie, 10, 289 (1896).

[2] Photogr. Correspondenz, 1885, 359.

[3] Hübl: Die Collodium-Emulsion, 70.

in a solution of the dye, not only is the silver bromide dyed but of course the gelatine or the collodion also. These dyed media then act as a screen for certain rays and modify the action of the sensitizing band. The position and form of this latter depend therefore on the more or less powerful sensitizing of the silver bromide which determines the breadth of the band. It also depends on the coloring of the film which may cause a weakening, a narrowing or a division of the sensitizing band.

"The spectroscopic examination of dyed silver chloride and silver bromide from collodion emulsions shows that the color of the silver salt determines the photographic action of the plate. These experiments have also shown that the absorption spectrum of dyed silver bromide does not differ materially in most cases from that of the dye in dry films. In consequence, the position of the maximum sensitizing corresponds, as a rule, very closely with the maximum absorption of the dye. It is only certain dyes, such as eosines for instance, which dye silver bromide with a color differing perceptibly from that of the dry dye. In this case it is the color of the silver bromide which determines the position of the sensitizing band.

(a) Cyanine

"Silver bromide and silver chloride are dyed by cyanine. In plates freed from an excess of the dye, the sensitizing band corresponds almost exactly with the absorption band of the dye. In plates with an excess of dye the sensitizing effect is modified by the screening action. One meets these [modified sensitizing bands] in collodion emulsions, and in gelatine plates which have been sensitized with an alcoholic cyanine solution. If one adds a cyanine solution to the liquid gelatine emulsion or if one bathes the plates in a solution diluted with a great deal of water, the gelatine is dyed a reddish-blue and shows a broad uncertain absorption band with two weak maxima, one between C and D, the other between D and E. In this case the previously mentioned screening action is of course not to be detected. Similar differences are to be found with other dyes insoluble in water.

(b) Eosine

"If one brings silver chloride, precipitated with an excess of chloride, into a dilute eosine solution, it is dyed a bluish-red and keeps this color even though it has been rinsed in a silver nitrate solution. Silver bromide acts in the same way. The spectroscopic investigation of these substances shows that the coloring is due to silver eosine.

"As a matter of fact, plates dyed with eosine or with silver eosine show the same absorption band. It must be kept in mind however that silver eosine is also a chemical sensitizer and that an excess of it causes a more powerful action than does eosine, and that therefore there is a more rapid spreading of the band in both directions. The absorption spectrum of eosine yellow [sodium eosine] is given in Fig. 1[1] and that of silver eosine in Fig. 2.[1] The latter corresponds to the sensitizing band in plates dyed with eosine or silver eosine, when there is only a very slight excess of dye.

"If the film carrying the silver bromide is also dyed, the screening action of the dye makes itself manifest in several ways, depending on whether eosine or silver eosine is the dyeing agent. In the first case we get the sensitizing curve in Fig. 3,[1] while with dry plates dyed with silver eosine the forms of Fig. 4[1] and Fig. 5[1] appear, depending on the amount of the dye used.

"This gives a most simple explanation for the fact, so often observed, that eosine and silver eosine sensitize for different portions of the spectrum."

Some of the peculiarities of stained silver bromide are brought out in the following quotation from v. Hübl.[2]

"If one precipitates silver bromide from an aqueous solution with an excess of bromide, separates the precipitate by filtration, moistens one portion of the precipitate with a

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[1] [Not reproduced in this article.]

[2] Jahrbuch der Photographie, 8, 189 (1894).

dilute silver nitrate solution, washing out the excess of the latter with distilled water, one gets two samples of silver bromide which, as everybody knows, behave differently photographically. For simplicity's sake we will designate these two forms as (*Br*) and (*Ag*).

"If one pours an eosine solution over these two substances, the silver bromide (*Ag*) is dyed a deep red while the silver bromide (*Br*) appears colorless if one washes the solution of the dye off with alcohol or water. Dissolved silver eosine on the other hand dyes both samples red. On treating with a potassium bromide solution, the reddened silver bromide is decolorized. The presence of soluble bromides therefore prevents the dyeing of silver bromide by eosine.

"If one treats a collodion emulsion, containing an excess of bromide, with eosine and exposes the moist plate to the spectrum, there is no sensitiveness to the yellow-green rays. This sensitiveness appears at once, however, if one removes the excess of bromide with silver nitrate.

"If one treats the two kinds of silver bromide with alcoholic cyanine solution, the silver bromide (*Ag*) is dyed an intense grayish-blue, while silver bromide (*Br*) assumes a light pink color. A solution of potassium bromide or of silver nitrate decolorizes the blue silver bromide. The sensitizing action of cyanine is in accord with this phenomenon.

Collodion emulsions, which contain silver bromide (*Br*), are not sensitized by cyanine even in presence of chemical sensitizers. If one adds a trace of silver nitrate, however, the orange-sensitiveness appears, but disappears again the moment there is present even the slightest excess of silver nitrate. A similar effect is to be noticed with quinoline red. Dry gelatine films, and perhaps also collodion emulsion films, act as differently, cyanine being a sensitizer even in presence of silver bromide (*Br*).

"From these experiments we may draw the following conclusions of importance to the theory of color sensitizers:

(1) In order that a dye may act as a sensitizer, it must color the silver bromide grain or at least come in close contact

as solid with the silver bromide. The presence of the dye in the still moist binding material is not sufficient.

(2) The combination between the dye and the silver bromide must, in most cases be attributed to molecular attraction.

"These experiments are of importance for the practice of orthochromatic photography because they show the importance of chemically pure dyes. The use of preparations containing iodides as impurity may lead to serious mistakes especially in research work."

Some other interesting results on the relation between the dyeing of the silver bromide and the resulting sensitiveness for the less refrangible rays are brought out in a later paper by v. Hübl.[1]

"Silver bromide, prepared with an excess of bromide and washed with great thoroughness, was tested with dye-solutions under different conditions, and the intensity of the dyeing noted. Then the dye was used under the same conditions as sensitizer for a silver bromide collodion emulsion and the ratio (v) was determined between the sensitiveness to the less refrangible rays and the sensitiveness to the blue and violet. For this purpose I used a photometer scale covered with a yellow or a blue glass under which the plate was exposed during the burning of a magnesium ribbon of definite length.

COLOR OF SILVER BROMIDE	RATIO OF SENSITIVENESS, V
A. Eosine	**A. Eosine**
(1) Silver bromide is only dyed very slightly by an alcoholic solution of eosine.	(1) An emulsion treated with a solution of eosine gave $v = \frac{1}{4}$.
(2) If one adds water to the solution of the dye, the silver bromide is dyed distinctly pink.	(2) If one washes the plate in water before exposing it, then $v = 9$.
(3) In presence of silver nitrate the silver bromide is colored deep red.	(3) A weak silver bath increases v to 50.
(4) Presence of ammonia prevents the dyeing of silver bromide.	(4) Addition of ammonia to an emulsion dyed with eosine destroys completely the green-sensitiveness.

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[1] Jahrbuch der Photographie, 17, 128 (1905).

COLOR OF SILVER BROMIDE	RATIO OF SENSITIVENESS, v
A. Eosine	**A. Eosine**
(5) If one tests the dyed silver bromide with a potassium bromide solution containing alcohol, it is nearly completely decolorized.	(5) If an eosine collodion plate is placed in a potassium bromide bath, 1:50, and then washed, v becomes $\frac{1}{3}$.
(6) Sodium chloride solution decreases the intensity of the color but little.	(6) After bathing with sodium chloride solution and washing, v was 8.
B. Cyanine	**B. Cyanine**
(1) Alcoholic cyanine solution dyes silver bromide an intense greenish-blue.	(1) In an emulsion to which cyanine has been added, v is 40.
(2) Successive addition of ammonia causes gradual decolorization.	(2) On adding ammonia to an emulsion dyed with cyanine, v became 2.
(3) Potassium bromide solution plus alcohol decolorizes silver bromide.	(3) After treating in a potassium bath, 1:50, v became 4.
(4) Sodium chloride solution has only a very slight decolorizing action.	(4) A sodium chloride bath does not change the sensitiveness, $v = 40$.
C. Ethyl violet	**C. Ethyl violet**
(1) Alcoholic solution of ethyl violet dyes silver bromide bluish-green.	(1) For the sensitized emulsion, $v = 6$.
(2) On adding water the color became deeper and changed to a violet blue.	(2) If the plate is washed in water before exposing, v becomes 40.
(3) Ammonia has a decolorizing action.	(3) After addition of ammonia to the emulsion, v was $\frac{2}{3}$
(4) Potassium bromide has a decolorizing action.	(4) After treating in a potassium bromide bath, v becomes 3.
(5) Sodium chloride decolorizes but little.	(5) After treating in a sodium chloride bath, v became 20.
D. Quinoline red	**D. Quinoline red**
(1) Alcoholic solution of quinoline red dyes silver bromide pale pink.	(1) On sensitizing with quinoline red, v became $\frac{1}{2}$.
(2) When water was added, the color became more intense.	(2) After washing in water, v became 5.
(3) Potassium bromide plus alcohol, and also sodium chloride have a decolorizing action.	(3) If the plate is washed in a sodium chloride solution, v becomes $\frac{1}{8}$.
(4) Ammonia decolorizes the silver bromide completely.	(4) Addition of ammonia to the emulsion destroys its sensitiveness for the green.

"A surprising thing in all these experiments is the high sensitiveness of the plates for the less refrangible rays. This becomes intelligible however when one considers that a very powerful source of light was used, magnesium ribbon burning at a distance of ½ m.

"An explanation for the varying coloring power of the dyes under varying conditions is to be found in the modern theory of dyeing, according to which solids, such as the dyed silver bromides are looked upon as 'solid solutions.' Alcohol and water have different solvent powers for the dye, its degree of dissociation is different in the two liquids and is also affected by addition of different things to the solution. These factors govern the distribution of the dye between the two solvents, the liquid and the silver bromide. The applications of the laws may be obscured by mutual chemical action and by absorption phenomena. It is certainly not permissible to apply results with flocculent silver bromide and alcohol or water to an emulsion of silver bromide in collodion; yet the above results show that, on the whole, there is a close connection between the power of the dye to color silver bromide and its power of sensitizing, because everything which changes the intensity of the dyeing, also affects the sensitizing action."

We must next ask ourselves how sensitizers act. Ostwald is a bit pessimistic in regard to this. He says[1] that it is impossible at present to tell how the light absorbed by the dyes manages to act on the silver salt. Vogel[2] says that dyes which are to be used to sensitize salts of silver should fulfil the following conditions:

(1) It should be instable in the light. Cyanine is the most powerful sensitizer and it is also one of the least fast to light. Quinoline red stands next to this both in sensitizing power and in lack of fastness to light. After these come the eosines.

(2) It must also have as great an optical absorbing

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[1] Ostwald: Lehrbuch. allgem. Chem. 2nd Ed., 2, I, 1059 (1893).

[2] Handbuch der Photographie, 4th Ed., 1, 220 (1890).

power as possible. Thus cyanine absorbs much more than aniline blue and is also a much better sensitizer.

(3) It must not decompose the silver bromide in the plate.

(4) It must diffuse easily and equally through gelatine solutions or collodion (many dyes are not easily taken up by gelatine).

(5) The power to act also as a chemical sensitizer is desirable. Silver eosine is one of the best examples [of a sensitizer]. Dr. Albert proved that it increased the sensitiveness of collodion emulsion forty-fold and this is due chiefly to an increase in the sensitiveness to the yellow."

The theory of Grotthuss enables us to make a definite statement in regard to sensitizers, and one that differs to a certain extent from any of the previous ones. A sensitizer must be a depolarizer, directly or indirectly. It must be a reducing agent in the broad sense of the term or it must be changed into one by the action of light. In either case, the sensitizer is decomposed by the action of light on the sensitized plate. This is not in accordance with Eder's views. In one place Eder[1] says that "it is not necessary that the coloring matter should undergo any change." In 1896 his views had not changed materially.[2]

"Two other questions have recently come to the front again.

(1) The question whether the light-sensitiveness (lack of fastness to light) in itself has an influence on the magnitude of the sensitizing action on silver bromide. I have always answered this question in the negative.

(2) The question whether the dye is primarily changed chemically (decomposed) when a dyed silver bromide plate is exposed to light and whether the resulting reaction product of the dye causes the formation of the photographic image (reduction). This view was defended by Abney at one time. The two questions belong together

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[1] "The Chemical Effect of the Spectrum," p. 34 (1883).

[2] Eder: Jahrbuch der Photographie, 10, 166 (1896).

logically and many years ago Prof. Vogel attacked this view of Abney's. My own experiments had caused me to reject Abney's older hypothesis and Bothamley has recently worked at these two questions which are now being discussed in England."

I shall have occasion to discuss Bothamley's work a little later in this paper. It will be well first to see how Eder believed that sensitizers act. He has given his theory of the matter at great length[1] in an address delivered in Vienna, October 15, 1889, on the occasion of a celebration in honor of Daguerre.

"Modern optics rests completely and with overwhelming certainty on the undulatory theory of light. It appears desirable to explain all the photochemical phenomena including the working of the newly discovered color sensitizers according to this theory and to apply the modern views on the undulatory motion of light both to the vibrations inside the molecule, occurring in all substances, and to the absorption phenomena.

"In the present development of optics, the science of physics gives the means of measuring the vibrations inside the molecule and the spectroscopic investigations of Dr. Krüss and also of Hartley furnish us with the necessary starting point.

"The internal vibrations of the molecule are governed: (1) by those forces which act from molecule to molecule, the physical molecular forces; (2) by those forces which act from atom to atom, chemical forces which cause the chemical upbuilding or decomposition of the molecule.

"If an entering light-wave vibrates in unison with the internal vibrations of the molecule itself, the light-wave acts on the molecule and increases the amplitude of the vibrating molecule. The light-wave is thereby used up; it has done work. Kinetic energy can be converted into other forms of energy, and the absorbed light-wave, as I have already shown in a previous paper,[2] may cause chemical work, evolution of heat, etc. The first-mentioned phenomenon is thus explained. If we assume

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[1] Eder: Handbuch der Photographie, 2nd Ed., 1, 259 (1890).

[2] Photogr. Correspondenz, 1885, 360 from Sitzungsber. Akad. Wiss. Wien, Part II, December, 1884.

that the light-wave increases the amplitude of the vibrations of the molecule very much, then the breaking of the molecular bonds will take place when a certain limit is passed and we shall have a photochemical decomposition.

"According to the undulatory theory, the transmitter of the light, the ether, fills all the spaces between the atoms in the molecules of a substance, and, by the internal molecular movement of the substance, is thrown into equally rapid and equally large vibrations or rotations as those of which the vibrations of the molecules consist. A substance exposed to light takes up only those vibrations of the ether waves in its neighborhood which correspond to the actual or *possible* vibrations of its molecules.

If we call λ the spectroscopically determined wave-length of that ray of light which is most strongly absorbed by a substance, if v is the velocity of light (299,000 km/sec), and if n is the desired number of vibrations of the absorbing molecule, then we have the equation

$$n = \frac{v}{\lambda}.$$

In the case of absorbing substances which show an absorption for different rays of light, the *most intense* absorption is the important one to consider, for this is characteristic of the main vibrations of the molecule, just as—to use a good simile of Dr. Krüss—the most intense vibrations of a tuning-fork or of a string produce the characteristic fundamental note. With a tuning-fork the tone is louder, the greater the amplitude; with light the intensity becomes greater. One may conclude that a greater intensity in the absorption of light is caused by a greater amplitude of vibrations in the absorbing medium.

"Silver bromide in the form of gelatine emulsion shows a maximum absorption for light of a wave-length of 450$\mu\mu$; from this we calculate, by means of the formula, that the molecule of silver bromide requires 664 billionths of a second to perform a main vibration. As a matter of fact, light of that oscillation number acts the most powerfully on silver bromide. In other words, it increases the amplitude of the vibrations inside the molecules of silver bromide to such an extent that a decomposition of the molecules takes place, or begins and is carried further by the photographic developer so that a powerful reduction is effected.

"In addition, there are numerous minor vibrations which go on inside the molecule of silver bromide in such a way that silver bromide takes up light-waves of a longer or shorter period whereby light is absorbed. Since these minor vibrations are less violent, and therefore react less readily with the light-waves, a more intense light is necessary in order to increase the vibration and amplitude to such a point that a decomposition of the molecule takes place. In other words, silver bromide is only slightly light-sensitive for such rays. Thus light from the extreme red to the extreme ultra-violet is absorbed by silver bromide, but only to a slight extent and the photochemical reaction is correspondingly slight.

"The slight sensitiveness of silver bromide to red or yellow is well known; it becomes a little greater if the silver bromide is digested with ammonia, etc. Thus silver bromide is only slightly changed by a yellow-green light which has a wavelength of 563$\mu\mu$ (corresponding to an oscillation period of 531 billionths of a second).

"This light is also absorbed but slightly; the internal movement of the silver bromide molecule is in harmony with these rays of light only in regard to the minor vibrations and light with an oscillation period of 531 billionths of a second can only with difficulty increase the amplitude of vibrations of the molecule of silver bromide to the decomposition point of the atomic complex.

"Let us consider the effect of another chemical substance which forms an intimate combination with silver bromide—either chemically or by molecular attraction—and itself absorbs light having a wave-length of 563$\mu\mu$ and, from the formula, an oscillation period of 531 billionths of a second.

"Such a substance is the sensitizer, erythrosine, discovered by me. According to my spectroscopic examination an alcoholic solution of this substance absorbs most strongly light of a wave-length, 529$\mu\mu$, while silver bromide dyed with it absorbs light of a wave-length, 563$\mu\mu$.

"If now a yellow-green ray of light with a wave-length of 563$\mu\mu$ falls upon silver bromide dyed with erythrosine, it finds erythrosine molecules which vibrate most strongly in harmony with that light-wave and which absorb it. The light-wave by continued action may increase the amplitude of the vibrations of erythrosine molecule to the decomposition point and may for instance bleach the erythrosine by itself. On the other hand, the silver bromide molecule also present may be stimulated by the increased vibrations of dye and what were secondary vibrations of the silver bromide may be converted into main vibrations and may cause the decomposition of the silver bromide.

"This explains the observation that dyes, with narrow absorption bands and with the main vibrations of the molecule confined to a narrow region of the spectrum, usually are stronger sensitizers because the stimulation of the silver bromide molecule probably occurs more easily if there is a narrowly limited region of attack.

"Silver iodide is not readily sensitized by dyes, probably because it has a main vibration corresponding to the blue rays of the spectrum and the molecular movement is only very slightly, or not at all, in harmony with longer light-waves. Therefore the action of an added and absorbing dye appears to be too weak to increase the sluggish movements of the silver iodide molecules up to the point where the atom complex breaks down. The conditions are more favorable with silver bromide which has a general sensitiveness for different rays of light.

"From this we deduce the conclusion, which is confirmed by the experimental observations, that color sensitizers for silver bromide, which play such an important part in orthochromatic photography, always sensitize silver bromide in the neighborhood of those parts of the spectrum, which the dyes themselves absorb. They vibrate in harmony with the light rays absorbed by them, and the increased amplitude of the molecular vibrations of the dye causes an increase in the corresponding vibrations of the silver bromide whereby the light waves increase the internal molecular movement of the silver bromide up to the point of decomposition. *In this way the connection between the absorption of dyes and the photographic sensitizing is explained on the basis of the undulatory theory.*"

A theory, like this one of Eder's, may be right but it is not helpful. It is like a gas, which adapts itself to every external condition but which one cannot take hold of. One can account for anything by means of it because one is never committed to anything and one can always express any fact in terms of the theory. It is easy to prove that the absorption bands must coincide with the sensitizing bands; it is just as easy to prove that they do not.

According to Eder's view there is no reason that the dye should undergo any chemical change, it acting the part of a catalytic agent. According to the theory of Grotthuss the dye acts as a depolarizer and therefore must be changed. It is therefore desirable to determine whether the sensitizers are fast to light or not. The experiments of E. Vogel[1] on the light-sensitiveness of eosine colors are distinctly instructive.

"All the eosine dyes bleach in the light in a relatively short time. Thus paper dyed with tetra-iodfluoresceine (erythrosine) or tetrabromfluoresceine (eosine) loses its color almost completely through two hours' exposure to direct sunlight.

"To bring out any relation between chemical composition and light-sensitiveness, I proceeded as follows. Raw photographic paper, *i. e.*, pure, white paper without any wood pulp, was stained with a solution of the alkali salts of the eosine dyes.[2] When dry, the colored papers were placed under Vogel's photometer scales and exposed simultaneously to direct sunlight. In this way, the light-sensitive substances were arranged in the following list, those most fast to light standing at the head.

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[1] Wied. Ann., 43, 461 (1891).

[2] To prevent the presence of acid salts an excess of ammonia was always added.

Fluoresceine.
Dichlorfluoresceine.
Tetrachlorfluoresceine, chlorine in phthalic acid radical.
Tetrabromfluoresceine, bromine in phthalic acid radical.
Tetrachlortetrabromfluoresceine.
Octobromfluoresceine.
Tetrachlortetra-iodfluoresceine.
Tetrabromtetra-iodfluoresceine.
Dichlortetrabromfluoresceine.
Dichlortetra-iodfluoresceine.
Tetrabromfluoresceine, bromine in resorcinol radical.
Tetra-iodfluoresceine, iodine in resorcinol radical.

"The following conclusions may be drawn:

(1) The substitution of chlorine, bromine or iodine in the resorcinol radical or in the phthalic acid radical of the fluoresceine causes an increase in the light-sensitiveness, substitution in the resorcinol radical increasing it more than substitution in the phthalic acid radical.

(2) Iodine-substituted fluoresceines are more light-sensitive than the corresponding bromine-substituted fluoresceines.

(3) Substitution of chlorine or bromine in the phthalic acid radical of fluoresceines containing bromine or iodine in the resorcinol radical decreases the light-sensitiveness. Dichlortetra-iodfluoresceine is therefore less sensitive to light than tetra-iodfluoresceine; dichlortetrabromfluoresceine and tetrachlortetrabromfluoresceine are less light-sensitive than tetrabromfluoresceine."

E. Vogel[1] also studied the sensitizing of the eosine dyes, with the following results:

"All the eosine dyes act as sensitizers. The fluoresceines, with the halogen substituted in the phthalic acid radical, sensitize less well than those with the halogen substituted in the resorcinol radical.

"The fluoresceines with halogen both in the phthalic acid and in the resorcinol radical sensitize less well than the fluoresceines with halogen substituted in the resorcinol radical but better than the fluoresceines with the halogen substituted only in the phthalic acid radical.

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[1] Wied. Ann., 43, 467 (1891).

"All the fluoresceines containing iodine sensitize better than the corresponding chlor- or brom-fluoresceines.

"The silver salts of all the iodine dyes act distinctly better than the alkali salts of the same; they differ from the alkali salts especially in making the sensitiveness of plates stained with them extend farther into the red. The blue-sensitiveness is also less, relatively to the sensitiveness of the sensitized region.

"Of all the eosine dyes the best are tetra-iodfluoresceine (erythrosine) and di-iodfluoresceine. Less effective are the fluoresceines with iodine in the resorcinol radical and also chlorine, bromine or sulphur in the phthalic acid radical, such as dichlortetra-iodfluoresceine and tetrabromtetra-iodfluoresceine, also thiodichlortetra-iodfluoresceine.

"Much less effective are the fluoresceines with bromine in the resorcinol radical. Inferior to these are the fluoresceines with bromine in the resorcinol radical and with halogen substitutions also in the phthalic acid radical. Least effective of all are the fluoresceines with halogen substituted only in the phthalic acid radical, and the mother compound, fluoresceine.

"According to H. W. Vogel, those dyes sensitize the best which are the most sensitive to light. As a matter of fact, the best sensitizers, tetra-iodfluoresceine and di-iodfluoresceine, are among the most sensitive to light, while the fluoresceines with halogen substituted in the phthalic acid radical and fluoresceine itself are among the most fast to light and are also the poorest sensitizers. It is surprising now to note the essentially greater sensitizing power of the iodine-substituted fluoresceines over the corresponding bromine compounds, thus tetra-iodfluoresceine and tetrabromfluoresceine, tetrachlortetra-iodfluoresceine and tetrachlortetrabromfluoresceine.

"I believe that this fact can be accounted for as follows: All the fluoresceine derivatives, containing only chlorine or bromine (tetrachlorfluoresceine or tetrabromfluoresceine, for instance) or containing both chlorine and bromine (dichlortetrabromfluoresceine or tetrachlortetrabromfluoresceine, for instance) show a powerful fluoresceine.

"On the other hand, there is little or no fluorescence to be detected in the fluoresceine derivatives containing iodine only, or chlorine and iodine, or bromine and iodine (di-iod-, tetra-iod-, tetrachlortetra-iod-, or tetrabromtetra-iod-fluoresceine).

"The rays absorbed by a substance may be changed into fluorescence, phosphorescence, heat and chemical action. In the fluorescing eosine dyes a greater part of the absorbed light is used up in exciting fluorescence. In the eosine dyes which do not fluoresce, all the absorbed light can be converted into chemical action or heat. As a matter of fact, the eosine dyes with the strongest fluorescence are the poorest sensitizers.

"In the following list there are a number of fluorescing substances arranged according to the order of their fluorescence, with the dye having the strongest fluorescence at the head:

	Fluoresceine.
	Dichlorfluoresceine, substitution in phthalic acid radical.
Equal fluorescence	Tetrachlorfluoresceine, substitution in phthalic acid radical. Tetrabromfluoresceine, substitution in phthalic acid radical.
	Dibromfluoresceine, substitution in resorcinol radical.
	Tetrabromfluoresceine, substitution in resorcinol radical.

"If one compares these results with the data as to the sensitizing action of the eosine dyes, one finds *that the sensitizing power of the eosine dyes increases as the fluorescence decreases.*"

The following passage is also pertinent:[1]

"The objection to the eosines is that they do not absorb red light and therefore do not make the plate sensitive to red. In this respect cyanine, first introduced by the author, is decidedly superior. It is certainly the least fast to light of the dyes and therefore apparently superior to eosine. Unfortunately it does not form a silver compound as eosine does, and it decomposes spontaneously very easily, so that cyanine plates do not keep. Next to cyanine comes quinoline red, discovered by Dr. Jacob-

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[1] H. W. Vogel: Handbuch der Photographie, 4th Ed., 2, 171 (1894).

sen and first recognized by the author as a sensitizer. It gives a powerful sensitiveness in the green, yellow and orange, corresponding to its absorption. The author added to it $^1/_{25}$ of cyanine so as to increase the sensitiveness in the red. Plates thus dyed are known commercially as azaline plates. Quinoline is very stable in the dark. Unfortunately, cyanine, quinoline and azaline plates always need a yellow screen (ray filter) even for ordinary exposures."

Some experiments of Bothamley[1] have a distinct reference to the work of E. Vogel and are of more interest in their bearing on Abney's theory of sensitizing.

"Although large numbers of dyes have been examined since Dr. H. W. Vogel's discovery in 1873, very few exert any marked effect in making gelatino-bromide plates sensitive to the less refrangible rays of the spectrum. Only cyanin and the dyes of the eosin group (including the rhodamines), with perhaps malachite green, chrysoidine, and alizarin blue, can be said to exert any useful effect.

"The main points established by previous observers may be summarized as follows: (1) The dyes that act as sensitizers are readily affected by light when they are in contact with fabric, paper, etc.; (2) in order that a dye may act as a sensitizer it must have the power of entering into intimate union with silver bromide, forming a kind of 'lake;' (3) and it must show a strong absorption band for the particular rays for which it is to sensitize. Although these statements hold good for all the dyes that are known to act as sensitizers, it is important to observe that the converse is not necessarily true. Several dyes having all these properties show no appreciable sensitizing action.

"Experiments by Dr. E. Vogel on the rate of fading and the sensitizing action of the eosin dyes, led him to the conclusion that the order of sensitizing effect coincides with the order of fading when the dyes are exposed to light. The order in which Vogel places the dyes does not, however,

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[1] British Association Reports, 1895, 661.

correspond with the order of fading as observed in dyed fabrics, and the experimental method that he used is open to criticism.

"The author's observations on the fading of the various sensitizers, when exposed to light in contact with gelatin, led him to the conclusion, that although all the sensitizers are readily affected by light, the order of sensitizing effect does not necessarily correspond with the order of fading, whether the dyes belong to the same chemical group or not.

"There are two chief hypotheses as to the mode in which the dyes act, namely: (1) the view held by Abney that the dye itself is oxidized by the action of light, the oxidation product remaining in contact with the silver bromide; and when the plate is treated with the developer, the latter and the oxidation product acting simultaneously on the silver bromide bring about its reduction; and (2) the view first definitely formulated by Eder, and endorsed by Vogel, namely, that the energy absorbed by the dyed silver bromide is partially used up in bringing about the chemical decomposition of the silver bromide, instead of being almost entirely converted into heat, as when absorbed by the dye alone.

"The author has found that the less refrangible rays will produce a photographic image on the sensitized gelatinobromide plates, when they are immersed in powerfully reducing solutions, such as mixture of sodium sulphite and pyrogallol. This holds good for cyanin, the eosin dyes, the rhodamines, and quinoline red, whether the sensitizer has been added to the emulsion or has been applied to the prepared plate in the form of a bath. It is, therefore, impossible to attribute the sensitizing effect to any intermediate oxidation of the dye.

"Experiments with various reagents such as potassium bromide, potassium dichromate, mercuric chloride, and dilute hydrogen peroxide seem to show that the chemical nature of the latent image produced by the less refrangible rays on the specially sensitized plates is precisely the same as that of the latent image produced by the more refrangible rays in the ordinary way.

"Further proof in the same direction is afforded by the fact that the effect of the sensitizers extends to the production of a visible effect by the prolonged action of light.

"The balance of evidence is therefore greatly in favor of the view that the dye absorbs the particular group of rays, and, in some way which is not at all clear, hands on the energy to the silver bromide, with which it is intimately associated, and which is thereby decomposed.

"For the present, for want of a better word, the phenomenon might be distinguished as *photo-catalysis*, and the sensitizer might be described as a *photo-catalytic* agent. As yet no connection can be traced between the chemical constitution and the general properties of a dye, and its sensitizing action."

Commenting on this paper of Bothamley's, Eder[1] says:

"These arguments of Bothamley's are worthy of attention. An experiment which I performed a long time ago led me by an entirely different way to similar conclusions. A solution of cyanine which had become brown and decomposed by years of exposure to the light, served as an experimental starting-point. This solution obviously contained the decomposition products of cyanine caused by light and must therefore cause a reduction if it is mixed with silver bromide and the silver bromide subsequently developed. I spread the solution over dry plates in the dark and laid them in the developer but without perceptible blackening of the parts over which the solution had been spread. Exposing a cyanine solution to light and adding it to the developer had no effect. I feel myself justified therefore in assuming: that cyanine and the other dyes do not cause a color-sensitizing through any chemical decomposition of their own in the light; and that the true explanation is to be found in the theory of the sensitizing action as a consequence of increased molecular vibration, a theory which was first proposed by Vogel and which was further developed by me."

Bothamley's experiments are conclusive in regard to the

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[1] Jahrbuch der Photographie, 10, 167 (1896).

assumption that the dye is first oxidized by the light and that the oxidation product helps the developer reduce the silver salt. Since the theory of Grotthuss requires that the dye shall either be a reducing agent itself or shall be converted into a reducing agent by light, the most that Bothamley's experiments prove is that cyanine, the eosine dyes, the rhodamines and quinoline red do not become reducing agents by being oxidized by light. On the other hand, Abney's experiments with the cyanine emulsion (p. 332) which he exposed to light, covered with silver bromide and developed, show that the decomposition product of cyanine is a reducing agent. In this case, Eder's experiment with the old cyanine solution is futile, because any reducing agent would have been oxidized long before the experiment was tried.

The question therefore is whether the action of light on these dyes is a reducing one or an oxidizing one. E. Vogel[1] has made the following experiments on erythrosine.

"Equally strong, very dilute solutions of tetra-iodfluoresceine in water were treated, part with sodium hydroxide and hydroxylamine hydrochloride, part with sodium hydroxide alone, and part with hydrogen peroxide.

"Portions of each of the three solutions were kept in the dark as a check while the remaining portions were placed in test-tubes and exposed to the sunlight. After about two hours' exposure to the sun the result was as follows. The solution containing hydrogen peroxide showed no visible change. The solution containing sodium hydroxide alone had become a little paler but was only slightly changed; the same was true of a neutral solution. The solution containing hydroxylamine, however, was entirely changed; the tetra-iodfluoresceine was reduced by the joint action of hydroxylamine to ordinary fluoresceine. In aqueous solution tetra-iodfluoresceine shows no trace of fluoresceine. After an exposure of ten to fifteen minutes to the sunlight, the appearance of fluorescence can be noticed in a solution con-

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[1] Wied. Ann., 43, 462 (1891).

taining sodium hydroxide and hydroxylamine. On further exposure to light the fluorescence becomes stronger until finally all the tetra-iodfluoresceine is reduced to fluoresceine. The solutions kept in the dark were entirely unchanged.

"That the reduction of tetra-iodfluoresceine by light in presence of hydroxylamine is not merely a result of the heating action of the sun's rays is shown by the fact that the solution when kept in the dark, does not change on being heated. All the bromine- and iodine-substituted eosine dyes behave like tetra-iodfluorescence when exposed to sunlight in presence of hydroxylamine. They are reduced to fluoresceine."

Gros[1] found that the fluoresceine derivatives absorbed oxygen when they were bleached in an atmosphere of oxygen by light. From this he concludes that these colors are oxidized by light. No reference is made to the work of E. Vogel and the results can be explained just as well on the assumption that light removes the halogen partially or completely and that the reducing agent, thus formed, takes up oxygen. There is thus no real contradiction between the experiments of E. Vogel and those of Gros. The work of the latter is really most satisfactory as a confirmation of the theory of Grotthuss in its application to the sensitizing of photographic plates by dyes.

There is another side to the matter. While eosine is bleached by reducing agents, it is also bleached by an acid permanganate solution. It is therefore possible that a direct oxidation took place under the conditions which Gros had in his experiments. Such a hypothesis is rendered plausible by the experiments of Straub[2] to which my attention was called by Professor Orndorff. Straub found that the reaction between a potassium iodide solution and oxygen under the influence of light was accelerated by the presence of eosine. The eosine appears to act only as an oxygen carrier, Straub assuming the intermediate formation of an "eosine peroxide."

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[1] Zeit. phys. Chem., 37, 157 (1907).

[2] Archiv. exp. Path. und Pharm., 51, 383 (1904).

It is possible that there is a reduction by light in this case followed by an oxidation, but we really don't know anything about it. What is needed is a careful study by some one of the chemistry of eosine and of erythrosine.

The results of E. Vogel have been confirmed by experiments made in my laboratory by Mr. Schluederberg who tried other reducing agents, less energetic than hydroxylamine. This is the first authentic case of an organic dye being reduced by light. The possibility of such a case was predicted by Ostwald who apparently did not know that his prediction had been fulfilled before it was made.

Referring to Chastaing's hypothesis that organic substances are oxidized by light and that salts are reduced by violet light and oxidized by red light, Ostwald[1] says:

"Chemical changes due to light cannot be classified solely under oxidation and reduction processes because oxygen does not always play a part. The assumption is also unscientific that a purely artificial classification of substances as organic and inorganic, made chiefly for didactic purposes, corresponds to a radically opposed photochemical behavior. It will not be difficult to show that oxygen-rich substances, like the nitro compounds for instance, are reduced by light if they are light-sensitive. The reaction is determined qualitatively by the chemical nature of the light-sensitive substance and not by the quality of the light."

The theories in regard to the sensitizing action of dyes, between which we have to decide are those of Abney, Eder and Grotthuss. Abney's view that the dye is oxidized by the light is overthrown by E. Vogel's experiment that the eosines are reduced by light and by Bothamley's experiment that the sensitizing action persists in presence of a solution of a reducing agent. Eder holds that the dye acts as a catalytic agent though he does not use this phrase. This theory does not account for the fact that some dyes stain silver bromide and are not sensitizers. It does not account for the fact that

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[1] Lehrbuch allgem. Chemie, 2nd Ed., 2, I, 1083.

all sensitizing dyes are light-sensitive. It is overthrown by Abney's experiment in which the silver bromide was added after the cyanine had been exposed to light.

The Grotthuss theory requires that the sensitizers should be depolarizers. They must be decomposed by light and must either be reducing agents or must be converted into reducing agents by light. It is not necessary that the order of light-sensitiveness should be identical with that of the sensitizing power. This latter depends on the potential while the rate of decomposition depends also on the unknown "chemical resistance." On the other hand, a general approximation between the light-sensitiveness and the sensitizing power is to be expected and is found. Dyes, which stain silver bromide and which are not depolarizers, directly or indirectly, are not sensitizers. Since we know that cyanine and the eosines are reduced by light, it is not surprising that reducing agents do not destroy the sensitizing power. Abney's experiment with cyanine follows at once now that we know that light converts cyanine into a reducing agent. Instead of the action of sensitizers being a mysterious one, it is a matter of course if one applied the theory of Grotthuss.

The general results of this paper are:

(1) The maximum of the absorption band for dyed silver bromide coincides with the maximum of the sensitizing action for the same dye.

(2) It is the absorption band for dyed silver bromide which counts and not the absorption band for dyed gelatine.

(3) Sensitizers are depolarizers, directly or indirectly.

(4) All sensitizers are light-sensitive but the light-sensitiveness and the sensitizing power need not run strictly parallel.

(5) Sensitizers are either reducing agents in the broad sense of the term or are converted into reducing agents by light.

(6) Cyanine and the eosine dyes are reduced by light.

(7) Light sets free halogen from the eosine dyes.

(8) Cyanine and eosine dyes are converted into reducing agents by light.

(9) There is no connection between sensitizing power and fluorescence.

(10) Eder's theory of molecular vibration cannot account for Abney's experiment with cyanine plates to which the silver bromide was added after the exposure to light.

(11) The electrochemical theory of light, first proposed by Grotthuss, accounts for all the known facts in regard to sensitizers.

Cornell University.

NEW BOOKS

Immunochemistry. *The Application of the Principles of Physical Chemistry to the Study of the Biological Antibodies. By Svante Arrhenius. 13×19 cm; pp. ix + 309. New York: The Macmillan Company, 1907. Price: $1.60 net.*—The whole book is summed up by Arrhenius in the preface as follows:

"The following pages contain a summary of six lectures on the Immunity Reactions delivered at the University of California, in Berkeley, California, during the summer session of 1904. The object of the lectures was to illustrate the application of the methods of physical chemistry to the study of the theory of toxins and antitoxins. The idea that the reciprocal action of toxin and antitoxin is of the same nature as a chemical reaction is nearly as old as the study of these phenomena, which was inaugurated by the discovery of the diphtheria antitoxin by Behring and Kitasato in 1890. The German School, led by Ehrlich, the renowned Director of the Prussian Serum Institute in Frankfort-on-the-Main, has in particular done much work in support of the opinion that the interaction of toxin and antitoxin is of the nature of a chemical reaction; whereas the French school, led by Metschnikoff, tried to show that the effect of an antitoxin is chiefly of physiological order, an antitoxin was supposed to stimulate in some way the organic tissues in their struggle against the attack of the poison.

"When Ehrlich succeeded in showing that the agglutinating action of ricin upon red corpuscles (erythrocytes) suspended in a physiological salt-solution (0.9 percent NaCl) is inhibited by the antibody—the antiricin—the notion that a physiological effect is executed by the antibody was abandoned by most scientists. Although I adhere to the chemical school, I cannot say that the proof of Ehrlich is quite convincing, since the erythrocytes may well be regarded as "living" even after their separation from the blood of the animal. The further fact stated by Ehrlich, namely, that approximately the *n*-fold quantity of a toxin requires the *n*-fold quantity of antitoxin for its neutralization, may be regarded as a more convincing proof against the physiological hypothesis. The chemical hypothesis is now generally accepted, and has been adopted recently by Bordet, who originally expressed ideas similar to those held by Metschnikoff.

"Nevertheless, many difficulties to the chemical hypothesis remained. Nothing was more natural, therefore, than that the further elucidation of the problem should be sought through the aid of the modern theories of solution. To this end, Madsen and Ehrlich invited me to join in their work. My work with Madsen in the Copenhagen Institute enabled us to fix upon a simple explanation of the chief difficulty exhibited by the so-called phenomenon of Ehrlich. The Chief of the Frankfort Institute was so deeply interested in the progress of these studies that he invited me to work in his Institute on the chemical behavior of compound haemolysis. In this case, also, it was determined that the laws of equilibrium found their application. It would seem, therefore, that the adherents of the chemical hypothesis should have felt wholly satisfied with the results. However, one of the strange incidents with which the history of science is replete occurred. In our explanation of the investigated phenomena, especially regarding the diphtheria toxin, Madsen and I, in accordance with the usual rule in the exact sciences, tried to employ as few hypotheses as possible, and in this we followed the example of Bordet. We tried to show that the phenomena observed might be explained on the supposition that diphtheria toxin is a simple substance which slowly decomposes into an innocuous material that still neutralizes antitoxin. In his explanation, Ehrlich had previously assumed the presence in the diphtheria poison of a large number of poisonous substances of different strength. Now, Ehrlich did not wish to yield this explanation, which he regards the principal point in his doctrine; and therefore, he and his numerous pupils raised a number of objections to the treatment of this branch of science in accordance with the modern theories of chemistry. Thereupon Biltz, encouraged by Ehrlich, took up and elaborated the old idea of Bordet, which had been abandoned by this prominent savant in favor of the chemical hypothesis, and suggested that antitoxin does not react chemically with toxin, but behaves about in the same manner as a dye when it becomes fixed in a fibre.

"Some of these recent objections to the ideas brought forward in the lectures, have been taken here into consideration, notwithstanding that they have appeared since the lectures were delivered. In the same way, much recent work, especially by Madsen and his pupils (*in large part as yet unpublished*), bearing upon the velocity of reactions, has been given consideration in the following pages. And the recent work of Hamburger on precipitins has been made use of in the final chapter.

"I have given to these lectures the title "Immuno-chemistry," and wish with this word to indicate that the chemical reactions of the substances that are produced by the injection of foreign substances into the blood of animals, *i. e.*, by immunisation, are under discussion in these pages. From this it follows also that the substances with which these products react, as proteins and ferments, are to be here considered with respect to their chemical properties. And for the purpose of a clarification of ideas, other substances that behave in an analogous manner will be given a consideration in the discussion.

"It is evident that the objection recently raised by Ehrlich and Sachs to this manner of investigation, namely, that it does not enter upon the mode by which the living body produces these so-called antibodies, is quite true. An investigation of the chemical relations of toxin and antitoxin need not carry with it an elucidation of the synthesis of the antitoxin. But I fancy that there are many who are so deeply interested in the chemical behavior of these substances that they will find an investigation of this question well worthy of study. And for myself, furthermore, I believe that the physiological side of the problem, alluded to by Ehrlich, will not find a satisfactory solution until the more simple chemical aspect is elucidated.

"The chief purpose of theoretical considerations is to afford clear and concise ideas of the observed facts. They thereby stimulate scientific research to a high degree. I venture to hope that the reader of the following pages will find that the theoretical views advanced by myself in this branch of science have fulfilled their rôle in a most satisfactory manner during the few years that they have been employed. I am glad to say that during these few years a large experimental material has been produced, which shows that the chief lines pointed out by theory are closely congruent with the facts; and this material has been produced almost exclusively in order to verify the said theoretical considerations. These have, therefore, already been of great scientific use, and yet this is only a small part of what may be expected. The reader will have frequent opportunities to compare the different scientific points of view that are connected with the theoretical views here exposed with those founded on other considerations."

One would like to quote nearly the whole of this admirable book. The following passages from pp. 18, 31, 35, 151, 157, 177, 255, 285, and 299 will suffice however to give a pretty clear idea of the contents of the book.

"As has been stated, many of the substances with which we deal in serotherapy, are rather unstable. This instability is very different in different cases. Sometimes (*e. g.*, for snake-venom) the toxin is more stable than the antitoxin; in the other cases (*e. g.*, for diphtheria and tetanus poison) the converse holds true. The snake-venom resists, as Calmette showed, an elevation to the temperature to 68° C., which, however, destroys its antitoxin, the antivenin, in aqueous solution. This circumstance was used by Calmette to separate the poison from the antivenin; after heating a mixture of the two a poisonous solution remained. According to more recent investigation of Martin and Cherry, this experiment is not successful if the mixture is held at the temperature of the room for more than thirty minutes before the heating is done.

"As Martin and Cherry intimate, the simplest explanation of this behavior is that the snake-poison and the antivenin require a certain time to react with each other. Hence, if the mixture is heated to 68° for ten minutes before the reaction has practically reached the end-value, the free antivenin is destroyed, and after the heating the mixture contains some free poison.

"The experiments of Calmette yield, therefore, no evidence for his conclusion that the binding of snake-venom by antivenin is a reversible process, whereby as soon as the free antivenin is destroyed, its compound with the poison is dissociated with the production of new quantities of poison and antivenin. The same comment may be made regarding the decomposition, by boiling, of the innocuous mixture of a poison generated by the *Bacillus pyocyaneus* and its antitoxin. After the boiling, the poison which is stable at that temperature, remains in the solution, while the more unstable antitoxin is destroyed, as Wassermann has shown.

"But there are many cases that demonstrate reversible processes between analogous substances against which no such objections can be upheld. One of the most remarkable of these processes is used for the production of the so-called immune bodies. (Ehrlich terms them "amboceptors.") If we inject a suspension of the erythrocytes of an ox into the vein of a rabbit, this animal after a certain time presents in its blood a haemolytic substance, which haemolyses the erythrocytes of the blood employed; *i. e.*, erythrocytes of the ox and perhaps of some nearly related species.

"If we heat blood-serum containing this haemolysin to 55° C. for about thirty minutes, we find that it loses its haemolytic power. It is said to be "inactivated." The haemolysin is evidently decomposed, but a fraction of it remains intact, as may be shown by adding the normal serum of a guinea-pig. After the addition of this innocuous serum, the inactivated serum has regained its power of haemolysing bovine erythrocytes. (The guinea-pig serum has in reality a slight haemolytic action on foreign erythrocytes, but in the experiment it need be used in such small dosage as to provoke in itself no visible haemolytic action.")......

"The influence of the time of reaction has also not been considered by Ehrlich as much as it should have been. Thus, for instance, Madsen and Dreyer had shown that a mixture of diphtheria-poison and its antitoxin, which is innocuous on subcutaneous injection into guinea-pigs, kills rabbits on intravenous injection. This phenomenon was explained by Ehrlich as due to the presence in the diphtheria-poison of a substance which could kill rabbits but not guinea-pigs. The recent investigations of Morgenroth show that the whole difference is due to the different modes of injection. A mixture which is innocuous to guinea-pigs when injected subcutaneously, may kill them when injected intracardially, *i. e.,* directly into the blood. The reaction between diphtheria-toxin and its antitoxin is not completed in less than a quarter of an hour, as Ehrlich supposed from his subcutaneous injections into guinea-pigs; according to Morgenroth's experiments, this reaction require several hours at 20° C. to reach the equilibrium. The experiments that gave different results for rabbits and guinea-pigs were carried out with nearly fresh mixtures of poison and antibody. If such a mixture be injected subcutaneously, it diffuses into the blood very slowly during several hours, and in the meantime the antitoxin binds the toxin. It is not necessary, with Morgenroth to introduce a new hypothesis; namely, that the tissues of the guinea-pig contain some catalytic agent reacting on the poison. The relatively high temperature (37° C.) of the animal, explains the relatively great velocity of the reaction. If, on the other hand, the mixture is injected into the veins, the poison is bound by the tissues of the animal before it has time to react with the antitoxin."......

"Morgenroth criticises a theory sketched by Nernst and developed by Biltz, Much, and Siebert, according to which the toxins are "adsorbed" to the "colloidal" antitoxins and thereafter destroyed. Morgenroth says, rightly, that this theory, "which as yet is void of any experimental basis," is completely disproved by his experiments.

"As will be *shown later on, the velocity of reaction of the different toxins* changes with temperature according to a law which was deduced from thermodynamical considerations, involving the validity of van't Hoff's law for solutions. The applicability of this law to the velocities of reaction of toxins may therefore be regarded as a new proof that the general laws bearing on the behavior of common *matter are valid even for the processes going on between the substances* studied in the phenomenon of immunity. No single proof has been adduced against the validity of these laws, and it seems to me very unphilosophical *a priori* to suppose that other laws should regulate the reaction of toxins and antitoxins, than those which govern the reactions of other substances."......

"Biltz, Much and Siebert, for two hours *shook* typhoid agglutinin with the following colloidal bodies: silicic acid or hydroxids of iron, zircon, and thorium. It was found that silicic acid had a noticeable, and the three other substances a much greater destructive action on the agglutinin. This seems to indicate that we have here to deal with a real chemical influence, which is not astonishing, as many different substances destroy agglutinins. For absorption, it is on the contrary, generally possible to show that the absorbed bodies (*e. g.*, dyes) exist on or in the absorbing substances, from which they may often be washed out. The authors have tried in vain to poison animals by the injection of hydroxid of iron which had been shaken with diphtheria poison or tetanospasmin, which, just as agglutinins, are attenuated by such shaking. If these poisons had been absorbed like agglutinins by the bacteria, *i. e.*, in a reversible way, then a strong poisonous effect should have manifested itself in the injected animals. But not a trace of the expected effect was observed. Biltz, Much and Siebert were then led to the conclusion that the hypothesis of absorption is not tenable.

"They have therefore taken up an idea incidentally suggested by Nernst for the explanation of the neutralization of toxins by their antibodies. The idea is not very different from that of Behring. (Cf. p.29). Let us suppose we have finely divided colloidal platinum (Bredig's "inorganic ferment") and hydrogen not very different from that of Behring. (Cf.p.29). Let us suppose finely divided colloidal platinum (Bredig's "inorganic ferment") and hydrogen peroxid. The peroxid condenses upon the fine metal particles and thereafter, it is decomposed. This would correspond to the condensation of a toxin, *e. g.*, ricin on the colloidal particles of its antibody, antiricin, and its subsequent decomposition. The antiricin itself should be slowly attacked by the ricin, just as the platinum, if it were oxidizable by the hydrogen peroxid. This explanation is incompatible with the fact that the ricin can be recovered after it is "neutralized," therefore, the neutralization cannot depend upon its destruction. It seems that the advocates and adherents of this idea (the schools of Nernst and of Ehrlich) had an intuition that it would conflict with experience. Evidently it agrees with the experiments in the shaking of poisons with colloidal hydroxids (except in that these substances are not chemically attacked by the poisons), but it does not harmonize with our experience with the reactions of bacteria to their agglutinins."...

"In other experiments, the bacteria used had been treated with serum containing agglutinin, nitrate of lead, ferric sulphate, alcohol, acids, or uranium acetate (which all agglutinate them), and thereafter, thoroughly washed until the wash-water did not show any reaction of the agglutinating substances. The bacteria treated in these different manners may be called sero, lead, iron, alcohol, acid, and uranyl bacilli respectively. The bacteria had then been altered so that they behaved in a different way to salt-solutions than did the original bacteria. On the addition of sulphuretted hydrogen to the bacteria treated with lead, these were coloured black, which proves that the bacteria had retained the lead in spite of the washing."

"This behaviour is to a high degree similar to that termed Ehrlich's phenomenon, observed in the neutralization of a toxin with its antitoxin. The first part of the antitoxin added neutralizes, generally speaking, a greater portion of the toxin than does the second equal addition, this a greater one than the third, and so forth. To explain this peculiarity (of diphtheria-toxin) Ehrlich supposes that the toxin is a mixture of many different 'partial toxins,' which possess different degrees of toxicity in equivalent quantities, and have a different affinity for antitoxin. If antitoxin be added, it at first neutralizes that part of the poison which has the greatest affinity, and which also is the strongest poison; thereafter that with the next greatest affinity, which also is the second in toxic strength, and so forth. At the end the very weakest portions appear for neutralization. Ehrlich designated these hypothetical 'partial poisons' with names coined from the Greek language, as prototoxin, deuterotoxin, tritotoxin, epitoxin, etc.

"If we apply Ehrlich's views to ammonia, this substance should, according to the experiment of neutralization by boric acid, be composed of different 'partial ammonias,' of which the strongest one should be neutralized first, the second strongest next, etc. Of course this complicated explanation cannot possibly be used for ammonia, which we know is a very simple chemical compound of high purity, but it was by Ehrlich and his pupils applied to other poisons quite generally, *e. g.*, to diphtheria-poison and tetanolysin, which, on neutralization as we shall soon see, behave in a manner very similar to ammonia."

' "Through absorption experiments Bordet proved that the same antiserum protects bovine erythrocytes against the immune-body contained in serum from a rabbit treated with bovine erythrocytes, and chicken erythrocytes against rabbit-serum treated with chicken erythrocytes. The same antiserum may therefore neutralize two entirely different immune-bodies, which are produced by the same species of animal (here rabbits). Therefore Bordet rejects the proof given by Ford and Wassermann, that the agglutinin to chicken erythrocytes, which is found in normal rabbit-serum, is identical with the said erythrocytes because both are neutralized by serum from chicken treated with rabbit erythrocytes.

"Bordet makes some remarks of great theoretical interest bearing upon the results of his experiments. Ehrlich and Morgenroth found that in the said combination of erythrocytes and immune-body it was possible to use alexin from goat-serum, although it had a weaker haemolytic action than that from guinea-pigs. They then made experiments with the neutralizing action of an antiserum produced by the injection of serum from rabbits treated with bovine erythrocytes into the veins of a goat. They found that this serum (in a given quantity) hindered the haemolysis by alexins from guinea-pigs, but not by that of goat-serum. But as the alexin from goats is much weaker, they used in this special case a much greater quantity of immune-body. Thereby they introduced not alone the immune-body in great quantity, but also the substances contained in normal rabbit-serum which are able to neutralize the antiserum. Bordet explains in this simple manner that the antiserum had no action in this case, and rejects the explanation of Ehrlich and Morgenroth, who assume that the different effect is due to the presence of two different kinds of immune-bodies in the preparation, of which the one gives compounds with the alexin from guinea-pigs and with the antiserum, the other with alexin from goats but not with the antiserum used. Evidently this proof is without validity. This is now conceded by Ehrlich, who believes, however, that other proofs are still valid."......

' "The binding of precipitin to casein may be judged, on the basis of the insignificant solubility of the compound, to be nearly complete if the two substances are present in equivalent quantities. If one of them is present in the fluid in excess, it is to a large extent carried down by the precipitate. Especially is this valid for precipitin. With the precipitable substance there is another perturbing influence, which is especially prominent with egg-albumen and which has its analogies in the behaviours of agglutinins and serum-precipitins. An excess of egg-albumen dissolves the precipitate, so that it is often observed that a given quantity of precipitin causes a precipitate with a weak but not with a stronger solution of egg-albumen. Even with casein this peculiarity may be observed, as Müller's later experiments indicate. The quantity of the precipitate produced by a given quantity of lacto-serum therefore increases at first with the quantity of casein added, and reaches a maximum in the neighborhood of the point where the casein added is equivalent to the quantity of lacto-serum, only to decrease thereafter and fall to zero at a point where the quantity of casein added is nearly double that corresponding to the maximum value; the determinations do not seem to be accurate enough to warrant more than an approximate valuation."......

"In the foregoing discussion it has been shown that the available observations conform to the laws deduced by physical chemistry for common chemical compounds. Therefore discussions as to whether toxins and their antitoxins, being defined as colloids, might be held not subject to these general chemical laws, and will possess but little interest until the assumed deviations from said laws are measured quantitatively. Any other method of procedure has a very hypothetical value."

The reviewer is not competent to determine to what extent the views of Arrhenius are correct. There is however no question but that this work of Arrhenius marks the beginning of a new era of what is called immuno-chemistry.

Wilder D. Bancroft

Stoichiometry. *By Sydney Young. Together with an Introduction to the Study of Physical Chemistry. By William Ramsay. 12 × 19 cm; pp. lxi + 381. New York: Longmans, Green and Co., 1908. Price: $2.00.*—In the preface the author says:—

"The determination of the relative atomic weights of hydrogen and oxygen is attended by great experimental difficulties, and, in arriving at a final decision as to the value to be adopted, chemists have placed even greater reliance on physicochemical investigations of the properties of the gases than on the purely chemical determination of the equivalent of oxygen.

"It was also in consequence of the determination of the specific gravities of nitrogen and oxygen by Lord Rayleigh and by Leduc that doubt was first felt as to the accuracy of the value found by Stas for the atomic weight of nitrogen, and it is chiefly owing to further investigations of the physical properties of these gases, and of other gaseous compounds of nitrogen, that the lower value has been definitely adopted.

"I have therefore thought it best, after describing the laws of chemical combination, to give a detailed account of the properties of gases before proceeding to a discussion of the methods of determining atomic weights.

"The importance of the generalizations of Van der Waals regarding corresponding temperatures, pressures, and volumes is now so fully recognized that no apology is, I think, necessary for the amount of space devoted to this subject, and to a description of the methods of determining the critical constants."

The headings of the chapters are: fundamental laws of chemical combination; general properties of gases; determination of atomic weights; accurate determination of atomic weights; the periodic law; the dissociation of gases and vapours; the properties of liquids; the kinetic theory of gases; properties of solids; mixtures; solubility and miscibility; properties of dilute solutions; dissociation and vaporization; the determination of molecular weights.

There are a number of interesting points in the book. Apparently Ramsay discovered Trouton's law seven years before Trouton did, and Pictet one year before Ramsay, p. 155. The author believes, p. 33, that there are some peculiarities about oxygen which cause the Boyle constant to vary at low pressures. "Again the fact that so many observers have obtained practically concordant results with hydrogen, but very discordant results with oxygen, seems to prove that there is some cause of disturbance other than ordinary experimental error, peculiar to the latter gas; but no satisfactory explanation of the anomalies observed by Bohr, Battelli, and Ramsay and Baly has yet been suggested. The law of Cailletet and Mathias is said to hold for normal pentane with perfect accuracy, p. 165, from 0° to the critical temperature 197.2°.

The author adopts D. Berthelot's value of 273.09° for the freezing-point of water, p. 51; but calls attention, p. 370, to the value of 273.13° calculated by Buckingham in a paper received too late to be considered in the text proper.

In one form of Lothar Meyer's table, p. 104, the author has arranged it so that "the electrochemical character of the elements is roughly indicated by the position of the symbols in the spaces they occupy, the electro-positive elements being placed to the left of the spaces, and the electro-negative elements to the right. Thus the symbol for caesium is placed far to the left of its space, that for fluorine far to the right."

The determinations of the atomic weight of nitrogen are of course discussed fully. As stated in the preface, it was the discrepancy between the values obtained from densities and the value of Stas which led to the further investigation of the matter and to the conclusion that Stas's figures were wrong. Since it seems probable from the determinations of Richards and others that there are distinct errors in nearly all of Stas's atomic weight determinations, it might be questioned whether the author was wise in laying so much stress on the accuracy of Stas's results and on the low probable error. An illustration taken from the work of Richards, would have been better.

The chapter on the determination of molecular weights is an excellent one though the reviewer believes that it could have been made better by including a reference to Ramsay's experiments with sodium and mercury. In a book of this size it is of course not possible to include everything but it seems a pity not to refer to a really important apparent discrepancy.

The book is a valuable one and is up to the high standard of the series.

Wilder D. Bancroft

Handbuch der Praktischen Elektrometallurgie. *(Die Gewinnung der Metalle mit Hilfe des elektrischen Stroms). By Albert Neuburger. 14 × 22 cm; pp. viii + 466. München: R. Oldenbourg, 1907. Price: bound, 14 marks.*—The subject is taken up under the following headings: iron, manganese; chromium; sodium; potassium; lithium; barium; strontium; calcium; beryllium; magnesium; aluminum; nickel; cobalt; copper; lead; silver; gold; zinc; cadmium; tin; bismuth; antimony; arsenic; mercury; columbium; tantalum; vanadium; molybdenum; tungsten; uranium; cerium; lanthanum; neodymium; praseodymium; gallium; thallium; zirconium; titanium.

One is always glad to welcome a new book on applied electrochemistry because a good one is needed very badly. This volume of Neuburger's is distinctly not the ideal book which one dreams about, but it has its good points and it will satisfy some needs.

In the preface the author states that he has given a good deal of space to the electric furnace preparation of iron and steel because of its present importance and because of there being no other satisfactory compilation of the outstanding literature. As a result, iron and steel take up the first third of the book. This part of the book is very satisfactory, though it seems excessive to devote eight pages to the Neuburger-Minet furnace if this is not actually in operation anywhere. Héroult's proposed electric blast furnace, p. 46, receives one page which would appear to establish the scale. Among the interesting minor bits of information in this section is the one, p. 22, that Stassano changed his furnace from a stationary to a rotating type to avoid having to briquette his ore. On p. 77, it should have been mentioned that Colby's patent for an induction furnace was obtained in 1890 and that he thus antedates Kjellin by a number of years. A recognition of this fact does not in the least detract from the real importance of Kjellin's work which consisted in demonstrating that an induction furnace could be used commercially in the manufacture of crucible steel.

The section on ferro alloys is not as good as that on iron and steel. There is nothing to show whether ferrosilicon and ferrochrome are made in resistance or in arc furnaces. Since silicon volatilizes only a couple of hundred degrees above the temperature at which ferrosilicon is formed, the ferrosilicon is not heated hot enough to tap and the process is a discontinuous one. With chromium no such difficulty occurs and ferrochrome is made by a continuous process On the other hand it is desirable not to reduce all of the chromium oxide to metal because then the product contains silicon, aluminum, etc. While on this subject, the reviewer would have welcomed a discussion of the relative merits of ferrosilicon and silicon in the iron industry.

On p. 152 the yield of sodium is given as about 70 percent but there is nothing to show that this means 35 percent efficiency as one would ordinarily calculate it. It is not quite clear why the Acker process should be included under the head of sodium alloys if the various mercury diaphragm processes for making caustic are omitted.

On p. 236 it seems hardly accurate to speak of the great similarity between the Hoepfner and the Browne processes for separating nickel and copper. They are both chloride processes, it is true, and the Browne process is a development from the Hoepfner process; but that is as far as one can go. Hoepfner leached the ores with cupric chloride while Browne let chlorine react with a copper nickel alloy. Browne's process was essentially one of electrolytic refining while Hoepfner was aiming at electrolytic extraction. It is not quite clear why the Hoepfner process for extracting copper from its ores should have suffered from the competition of the Siemens and Halske process, p. 258, since this latter process never became a commercial success.

The author tells us more about the preparation of magnesium, p. 196, than is to be found in any other corresponding book. Under aluminum he calls attention, p. 203, to the fact, usually overlooked, that the true or French bauxite has the composition $Al_2O_3.2H_2O$ while the American bauxite, so-called, is $Al_2O_3.3H\ O$. While the author refers to facts in regard to the manufacture of aluminum having become known through the legal battles between the Cowles Co. and the Pittsburgh Reduction Co. it seems probable that he has never seen the actual publications or he would have given some pictures of the aluminum furnace.

The German point of view appears in the statement on p. 273, that "In America the current density is kept pretty high in order to accelerate the process; but that in Germany on the other hand the usual current density is about 30 amperes per square meter electrode surface." Relatively speaking, the electrolytic refining of copper in Germany is negligible. It would have been instructive if the author had pointed out why the Germans use the particular current density that they do; but, in any case, the American conditions should have been given. There is nothing to show why the electrolyte in copper refining should be an acidified copper sulphate. Reference is made to Beadle's experiments with copper nitrate but they are not discussed and the absurd statement is made that 3-4 volts would be necessary. The Dietzel process is cited as a case of refining in nitrate solution but this is hopelessly misleading. In the Dietzel process there is a two solution cell and the silver is precipitated by copper outside the cell.

The series system of refining copper is treated in a very offhand way. On p. 270, it is stated that more copper is locked up in the tanks than in the multiple system; on p. 281 it is stated that there is more anode scrap with the series system than with the multiple system. No proof of these assertions is offered in either case. It is not explained, p. 282, why the high voltage between the terminal electrodes should cause heavy current losses. From another statement on p. 282, it looks as though the author thought that the electrodes were removed several times during a run and the cathode copper stripped from the anode portion. The author does not mention at all the real objections to the series system: that there are more anodes to be cast per ton of copper; that the anodes must be rolled; and that there is a great deal of manual labor necessary in connection with putting the anodes into the tanks and taking the cathodes out. The author also does not mention the real advantages of the series system: the lower voltage between plates; and the elimination of many of the contact losses.

The cut, Fig. 94, represents a multiple arrangement; but it is not the multiple arrangement that is actually used. It is possible that people still blow air into the cells at Goslar, p 275; but it certainly is not done in America. The reviewer has been unable to find any analyses either of anode or of cathode copper.

If the electrolytic refining of copper is given under the head of copper, it is not clear why the Moebius process for refining silver should not be given under silver instead of under gold, p. 358. Unless the unfortunate reader happens to be posted, he is likely to get the impression that the Dietzel process is more important commercially than the Moebius process. The reviewer finds it difficult to believe that anybody, refining silver by the Moebius method, would start with an electrolyte containing 40 grams Cu and 5 grams Ag per liter, p. 358. Incidentally, it may be remarked that the Moebius process with an endless belt, p. 357, has not been used in Denver since 1902.

On p. 350 the author gives a comparative statement of the cost of precipitation by zinc and by electrolysis. Unfortunately this comparison dates back more than ten years and the author does not tell us why it is that electrolytic precipitation is not more than holding its own in South Africa and has not really got a foothold in America.

It is a thankless task to pick flaws in a book like this; but it must be done if we are ever to get a really satisfactory book. It seems to the reviewer that a chapter on any electrolytic process should give: nature of containing vessel; composition of electrolyte; nature and composition of anode and cathode; distance between anode and cathode; temperature of bath; voltage, current, and electrical efficiency; arrangement of tanks, etc., and reasons why all these things are as they are, rather than some other way. We have a right to ask for all of these things, though it is a right which has never been recognized. If we could get all these things, all the other important details in regard to the manufacture might be considered as chemical engineering and might be reserved for a subsequent volume by somebody else. *Wilder D. Bancroft*

Untersuchungen über die galvanische Leitfähigkeit der Elektrolyte. *By Svante Arrhenius. (Ostwald's Klassiker der exacten Wissenschaften. No. 160.) Ueber-setzt von Anna Hamburger und herausgegeben von Otto Sackur. 12 × 19 cm; pp. 153. Leipzig: Wilhelm Engelmann, 1907. Price: bound, 2.50 marks.*—The original paper of Arrhenius is now readily accessible in this translation and it is a surprise to find how much the paper actually contains. Of course we have known for years that in it was Arrhenius's assumption that dissolved substances were present partly in an active form and partly in an inactive form. In addition we find an application of this assumption to equilibria in homogeneous and heterogeneous systems, an application to reaction velocities, a very satisfactory discussion of hydrolysis, and a clear account of the effect of ammonium carbonate on conductivity determinations with dilute solutions of acids or bases.

This volume is a most welcome addition to the series and it shows Arrhenius in a new light. A good many people have felt that the electrolytic dissociation theory would have been discovered by van't Hoff if Arrhenius had not nipped in ahead of him. It is quite clear however that the electrolytic dissociation theory was entirely the work of Arrhenius and that van't Hoff's work on solution merely gave Arrhenius valuable data on which he could test his theory.

Wilder D. Bancroft

Leçons sur la Viscosité des Liquides et des Gaz. *By Marcel Brillouin. Seconde Partie: Viscosité des Gaz.; Caractères généraux des Théories moléculaires. 16 × 25 cm; pp. 141. Paris: Gauthier-Villars, 1907.*—With his usual thoroughness, Professor Brillouin has brought together in systematic form, the present state of our knowledge of the viscosity of gases. In the first section of the book the methods of vibrating plates to which Maxwell made the essential contributions, is reviewed in detail. Then follows the work done with capillary tubes, used both at ordinary temperatures, for the investigation of questions relating to constitution and absolute values, as well as at high temperatures for the specification of the thermal coefficients. All complicated experimental devices are described by the aid of carefully drawn figures. Great impetus was given to these researches by the discovery (due to Sutherland) of an equation which reproduces the temperature relation with remarkable accuracy. The suggestions definitely put forth by the Reviewer (Wied. Ann., 36, 358 (1889)) of using the marked thermal variations for the measurement of high temperatures have not yet, however, been successfully practiced, though some progress has been made by Callendar.

The final part of the book (Livre IV) is a succinct digest of molecular theories propounded for the treatment of viscosity. Apart from its well-known uses as a distinctive constant viscosity yields a reasonable datum of molecular diameter. The book ends with a carefully drawn and suggestive conclusion, outlining the whole field of the researches reviewed. He has thus placed all who are interested in viscous flow, a subject in which the great advances still await the future, under a debt of gratitude. *C. Barus.*

Chemical Reagents, *their Purity and Tests. A New and Improved Text Based on and Replacing the Latest Edition of Krauch's "Die Prüfung der chemischen Reagentien auf Reinheit." By E. Merck. Authorized Translation by Henry Schenck. 15 × 24 cm; pp. vi + 250. New York: D. Van Nostrand Company. 1907. Price: $1.50* net.—In the preface, the author says: "The desire of American chemists to rid themselves of the misleading term. "C. P.," and to get in its stead definite statements as to the exact degree of purity of their reagents or the exact limit of the impurities, impelled the American Chemical Society, in 1902, to create a Committee on Purity of Reagents. In 1906 this committee advised against the publication of a book, because—to use their own language—"until further work is done and more data collected, such a work would be practically only a duplicate of the work of Krauch."

"It is evident that the work of the committee is being performed with most painstaking care; at the time of the last report the committee was working on 'perfecting a method for the accurate colorimetric determination of traces of iron.' It is evident, too, that if the collection of data regarding other tests than those for iron is pursued with the same painstaking care, the complete report of the committee will not be ready for publication for several years. My excuse for presenting this translation now lies, therefore, in the hope that, until the work of the committee appears, chemists will generally make acceptance of their purchases conditional upon their coming up to the specifications of purity prescribed by this translation.

"The additions mentioned by Dr. Krauch, in the preface he has kindly consented to write for this book, are limited to articles which are universally used here but do not seem to be so in Europe, and for which specification could be found in authoritative American publications. They are glacial acid 99.5 percent, 36 percent acetic acid, hydrochloric acid of a specific gravity of 1.050, nitric acid with one of 1.40, phosphoric acid with one of 1.057, 10 percent sulphuric acid, 28 percent ammonia water, 95 percent alcohol and glycerin of a 1.250 specific gravity. The slight changes obviously necessary in the text on account of these additions have been carefully made."

The book is the standard and as such is essential to everybody.

Wilder D. Bancroft

Thermochemistry. *By Julius Thomsen. Translated from the Danish By Katherine A. Burke. 12 × 19 cm; pp. viii + 495. New York: Longmans, Green and Co., 1908. Price: $2.50.*—The German translation has already been reviewed (10, 675), so it is only necessary to call attention to the appearance of the work in an English translation. *Wilder D. Bancroft*

THE EFFECT OF FERRIC SALTS ON THE RATE OF OXIDATION OF FERROUS SALTS, AND ON THE CATALYTIC ACTION OF THE LATTER.

BY W. F. GREEN

Experiments carried out in this laboratory by Miss C. C. Benson in 1902–1904[1] showed that the oxidation of ferrous sulphate by chromic acid is much retarded by the presence of ferric salts, and that the catalytic action of ferrous salts on the oxidation of iodides by chromic acid is likewise greatly diminished by the same reagent.

In the hope of throwing light on this remarkable case of negative catalysis, I have studied the effect of ferric salts on the rate of oxidation of ferrous salts by chloric acid and by oxygen and on the rate of oxidation of iodides by chloric acid and by bromic acid in the presence of ferrous salts.

I. Oxidation of ferrous chloride by chloric acid

The rate of this reaction has been studied by Noyes;[2] no effect of the ferric salt on the rate is apparent in his results; direct measurements, however, were undertaken to make sure.

The measurements were carried out in stoppered bottles, under carbon dioxide, in a thermostat at 30° C. as described by Noyes. The volume of the reacting solution was 250 cc in each case. The solution of ferrous chloride, free of ferric, contained 0.4148 equivalent (52.60 grams $FeCl_2$) per liter; the potassium chlorate 0.500 equivalent (10.21 grams $KClO_3$) per liter; while the hydrochloric acid was 1.022 normal, and the permanganate used in titration was 0.122 normal.

The reagents were present in almost equivalent quantities, and from the results of the measurements the "constant" K of the kinetic equation $dx/dt = K(A - x)^3$ was

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[1] Jour. Phys. Chem., 7, 1, 356 (1903).

[2] Zeit. phys. Chem., 22, 210 (1897).

calculated, in which A represents the geometrical mean of the numbers of equivalents of the three reagents present at the moment $t = 0$. In order to avoid "initial disturbances," the time of the first analysis was taken as zero for t and for x, the composition of the solution at that moment being calculated from the known quantities of the stock solutions used in making it up, and the result of the first analysis.

At the head of each table is given the number of equivalents of each reagent per liter at $t = 0$; under t the time from the first titration in minutes; under "titration" the number of cubic centimeters of permanganate used in titrating 25 cc of the reacting solution; under D the differences from the last column; under $x = \frac{0.122\,D}{25}$ the equivalents of ferrous salt oxidized per liter; and under K the constant calculated as explained above.

The reacting solution of Table 1 contained initially only the trace of ferric salt formed in the two minutes which elapsed between the time of mixing and the first titration. The solutions of Table 2 contained 20 grams ferric ammonium alum per liter; that of Table 3, 40 grams of the alum; and that of Table 4, 64 grams. The values of K are practically the same for all; in other words the ferric salt exerts no appreciable retarding influence on the rate.

TABLE 1

$Fe'' = 0.1169$, $Chl = 0.0925$, $Ac = 0.0947$, $(A = 0.1008)$, $Fe''' = 0$

Number	T	Titration	D	x	K
1	0	23.95	—	—	—
2	13	19.10	4.85	0.0237	0.054
3	30	15.90	8.05	0.0393	0.056
4	45	14.22	9.73	0.0475	0.056
5	60	13.05	10.90	0.0532	0.058
6	90	11.45	12.50	0.0610	0.060

TABLE 2

$\text{Fe}'' = 0.1179$, $\text{Chl} = 0.0935$, $\text{Ac} = 0.0957$, $(\text{A} = 0.1018)$, $\text{Fe}''' = 0.0416$

Number	T	Titration	D	*x*	K
1	0	24.15	—	—	—
2	12	20.10	4.05	0.0198	0.045
3	30	16.65	7.50	0.0366	0.048
4	45	14.77	9.38	0.0458	0.051
5	60	13.48	10.67	0.0521	0.053
6	90	11.80	12.35	0.0603	0.056

TABLE 3

$\text{Fe}'' = 0.1152$, $\text{Chl} = 0.0908$, $\text{Ac} = 0.0930$, $(\text{A} = 0.0991)$, $\text{Fe}''' = 0.0832$

Number	T	Titration	D	*x*	K
1	0	23.60	—	—	—
2	31	16.15	7.45	0.0364	0.048
3	60	13.50	10.10	0.0493	0.049
4	93	11.50	12.10	0.0591	0.057

TABLE 4

$\text{Fe}'' = 0.1145$, $\text{Chl} = 0.0901$, $\text{Ac} = 0.0923$, $(\text{A} = 0.0984)$, $\text{Fe}''' = 0.1330$

Number	T	Titration	D	*x*	K
1	0	23.45	—	—	—
2	31	15.85	7.60	0.0370	0.051
3	60	13.00	10.45	0.0510	0.055
4	93	11.00	12.45	0.0608	0.063

II. Oxidation of ferrous sulphate by oxygen

This reaction was studied here by Mr. J. W. McBain in 1901.[1] I used the method of working and of analysis described by him, and his apparatus for the preparation and storage of the solution of oxygen, which was saturated with the gas at 15.5° C and 758 mm barometer. The ferrous sulphate solution was freed from ferric salt by barium carbonate

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[1] Jour. Phys. Chem., 5, 623 (1901).

as described by Miss Benson;[1] it was kept under carbon dioxide and gave no red color with potassium sulphocyanate.

In every case the reacting solution contained 200 cc of 1.05 normal sulphuric acid[2] and 200 cc oxygen water per liter; the amounts of ferrous sulphate and ferric chloride in mols per liter are given at the head of each table. All experiments were carried out at 30° C.

The standard solution used for comparison in the colorimeter was made up fresh for each experiment, by mixing a solution containing 0.0966 gram $FeCl_3$ per liter of normal sulphuric acid, with its own volume of an aqueous solution of ammonium sulphocyanate containing 47.5 grams of the salt per liter.

In making an analysis, 25 cc of the reacting mixture were added to 12.5 cc of the ammonium sulphocyanate, and to this (except in the case of Table 5) 50 cc of water were added; 15 cc of the colored solution so prepared were placed in the colorimeter tube. Twenty-five cc 0.00459 normal ferric chloride thus treated matched 14 mm of the standard color if the 50 cc water had been added, 52.5 mm if it had not. In Tables 5 and 6 each analysis was made from the contents of a separate stoppered bottle; in Tables 7 and 8 samples were pipetted from a larger quantity.

In Tables 5 and 6 the differences are entered under "amount oxidized" in the last column. Their equality shows that the ferric salt has no influence on the rate. In the experiments of Tables 7*a* and 8*a*, immediately before the second analysis, ferric chloride was added to the reacting solution in such quantity that the amount added per liter was equal to the amount added per liter to the solutions of 7*b* and 8*b* respectively at the beginning of the experiment. The agreement between the results of the last three analyses in Tables 7*a* and *b* and 8*a* and *b* respectively shows that the presence of ferric chloride during the first seventeen hours of the reaction had no effect on the rate.

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[1] Jour. Phys. Chem., 7, 5 (1903).

[2] Except Table 5B where 250 cc acid was used.

TABLE 5

5(*a*)

$\mathrm{Fe}''' = 0$, $\mathrm{Fe}'' = 0.229$

No.	Time		Reading in mm.	Amount oxidized
	Hrs.	Min.		
1	0	07	5.0	—
2	3	02	23.5	18.5
3	5	33	35.5	30.5
4	23	25	60.0	55.0
5	28	06	64.0	59.0

5(*b*)

$\mathrm{Fe}''' = 0.0119$, $\mathrm{Fe}'' = 0.229$

No.	Time		Reading in mm.	Amount oxidized
	Hrs.	Min.		
1	0	07	7.5	—
2	3	02	27.5	20.0
3	5	33	36.5	29.0
4	23	25	59.5	52.0
5	28	06	68.0	60.5

TABLE 6

6(*a*)

$\mathrm{Fe}''' = 0$, $\mathrm{Fe}'' = 0.2384$

No.	Time		Reading in mm.	Amount oxidized
	Hrs.	Min.		
1	0	08	0.0	—
2	1	50	5.0	5.0
3	20	00	11.0	11.0
4	70	25	11.5	11.5

6(*b*)

$\mathrm{Fe}''' = 0.0119$, $\mathrm{Fe}'' = 0.2384$

No.	Time		Reading in mm.	Amount oxidized
	Hrs.	Min.		
1	0	07	12.0	—
2	1	50	16.0	4.0
3	20	00	21.0	9.0
4	70	25	23.5	11.5

TABLE 7

7(*a*)

No. 1, $\mathrm{Fe}''' = 0$; No. 2, $\mathrm{Fe}''' = 0.0238$; $\mathrm{Fe}'' = 0.2384$

No.	Time		Reading in mm.
	Hrs.	Min.	
1	0	03	0.0
2	17	30	34.5
3	22	54	48.5
4	43	15	88.0

7(*b*)

$\mathrm{Fe}''' = 0.0238$, $\mathrm{Fe}'' = 0.2384$

No.	Time		Reading in mm.
	Hrs.	Min.	
1	0	06	17.0
2	17	35	34.5
3	22	54	48.0
4	43	15	89.0

TABLE 8

8(*a*) No. 1, Fe''' = 0; No. 2, Fe''' = 0.0238; Fe'' = 0.1907

8(*b*) Fe''' = 0.0238, Fe'' = 0.1907

No.	Time		Reading in mm.	No.	Time		Reading in mm.
	Hrs.	Min.			Hrs.	Min.	
1	0	03	0.0	1	0	04	20.0
2	17	50	41.5	2	17	50	42.0
3	22	49	49.5	3	22	49	51.0
4	43	18	68.0	4	43	18	68.0

III. Catalysis of the reaction between chloric and hydriodic acids

This reaction has been studied here by Mr. W. C. Bray in 1902–3.[1]

He found that addition of a little ferrous salt greatly accelerated the rate. I have measured the effect of ferrous and ferric salts on the rate, and also the effect of ferric salt on the catalysis by ferrous.

In my experiments I followed Bray, working in stoppered bottles under carbon dioxide at 30° C. In every case the total volume of the reacting solution was 250 cc, containing initially 50 cc of normal hydrochloric acid, 50 cc of normal potassium iodide, and 10 cc half-normal potassium chlorate (p. 389); the iron is given at the head of the tables, the unit being 55.9 grams iron (ferrous or ferric) per liter. Fifty cc were removed for analysis, and titrated with hundredth-normal thiosulphate. In calculating the constant $K = 1/t \log_{10} (A/A - x)$ the time of the first titration, made within one minute of adding the iodide, was taken as $t = 0$; the amount of this titration was subtracted from all subsequent readings before entering them in the tables, and from 50.00 to give the value of A.

The results show that the reaction is greatly accelerated by both ferrous and ferric salts; that the acceleration is practically equal for equal amounts of iron independent of its

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[1] Jour. Phys. Chem., 7, 92 (1903).

state of oxidation; and that in solutions containing both ferrous and ferric salt, the effects of the two are additive. The presence of ferrous salt in the solution of Table 12, after standing for twenty-four hours, was shown by potassium ferricyanide.

TABLES 9 AND 10

9 $\mathrm{Fe} = 0$,				10 $\mathrm{Fe}'' = 0.0005$,			
No.	t	$A - x$	K	No.	t	$A - x$	K
1	0.0	50.0	—	1	0.0	49.75	0.0
2	35.0	0.1	0.000034	2	35.0	48.00	0.00045
3	97.0	0.3	0.000018	3	95.0	45.00	0.00046
4	1200.0	1.52	0.000011	4	116.0	44.20	0.00044
				5	1197.0	13.80	0.00046

TABLES 11 AND 12

11 $\mathrm{Fe}''' = 0.0005$				12 $\mathrm{Fe}'' = 0.0005$, $\mathrm{Fe}''' = 0.0005$			
No.	t	$A - x$	K	No.	t	$A - x$	K
1	0.0	44.30	—	1	0.0	44.4	—
2	30.0	43.00	0.00043	2	15.0	43.0	0.00093
3	77.0	40.30	0.00053	3	30.0	41.5	0.00098
4	90.0	39.65	0.00054	4	45.0	40.2	0.00096
5	1159.0	7.15	0.00060	5	62.0	38.9	0.00091
				6	92.0	36.6	0.00091
				7	105.0	35.3	0.00095
				8	150.0	33.2	0.00085

TABLES 13 AND 14

13 $\mathrm{Fe}'' = 0.001$				14 $\mathrm{Fe}''' = 0.001$			
No.	t	$A - x$	K	No.	t	$A - x$	K
1	0.0	48.40	—	1	0.0	44.50	—
2	15.0	46.95	0.00087	2	15.0	43.10	0.00093
3	30.0	45.40	0.00092	3	30.0	41.70	0.00094
4	45.0	44.00	0.00092	4	45.0	40.15	0.00100
5	62.0	42.40	0.00093	5	62.0	38.65	0.00099
6	92.0	39.90	0.00091	6	92.0	36.10	0.00099
7	105.0	38.90	0.00090	7	105.0	35.00	0.00099
8	150.0	35.45	0.00090	8	150.0	31.45	0.00101

IV. Catalysis of the reaction between bromic and hydriodic acids

This reaction has been studied here by Mr. Clark[1] in 1904–5, and I followed his method of working, mixing the iron salts with the iodide and acid before adding the bromate.

In each experiment the total volume of the reacting solution was 250 cc, containing 10 cc decinormal potassium iodide, 20 cc decinormal hydrochloric acid, and 10 cc decinormal potassium bromate (one sixtieth formula weight per liter); the iron present is given at the head of each table in formula-weights Fe (ferrous or ferric) per liter. In each experiment the temperature was 30° C, and the duration of the reaction thirty minutes. The numbers in the tables give the volume (cubic centimeters) of hundredth-normal arsenite oxidized in two or four duplicate experiments, the total reduction of the bromate corresponding to 100 cc arsenite.

Except where the presence of large amounts of ferric salt interfere with the titration, the results of the duplicates are in fair agreement; they show that, as in the case of chloric acid, equal weights of ferrous and ferric iron have the same effect on the rate, and that in mixtures as well the acceleration depends only on the total amount of iron present.

TABLE 15

$t = 30$. Readings in cc. of n/100 sodium arsenite

No.	$Fe = 0$	$Fe'' = 0.0002$ per liter	$Fe''' = 0.0001$ per liter	$Fe'' = 0.0004$ per liter	$Fe'' = 0.0002$ per liter	$Fe'' = 0.0002$ $Fe''' = 0.0001$ per liter
1	4.86	8.92	8.86	11.67	9.80	10.04
2	4.95	8.94	8.83	11.92	11.32	10.83
3	—	—	—	11.65	10.94	10.45
4	—	—	—	11.89	10.24	10.44

Conclusion

The oxidation of ferrous salt by chloric acid, and by oxygen, is not retarded by addition of ferric salt; neither is the catalytic action of ferrous salt on the oxidation of hy-

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[1] Jour. Phys. Chem., 10, 679 (1906).

driodic acid by chloric or bromic acids. The negative catalysis which ferric salts exert on the oxidation of ferrous salts by chromic acid, and on the liberation of iodine in solutions containing ferrous salt, chromic and hydriodic acids, thus stands alone.

Ferric salt is without effect on the rate of oxidation of ferrous salt by chloric acid and by oxygen. Both ferrous and ferric salts accelerate the liberation of iodine in solutions containing chloric or bromic acid and hydrogen iodide, the rate depending merely on the amount of iron present, and not on its state of oxidation.

These measurements were carried out at the suggestion of Prof. W. Lash Miller in the winter of 1904-5.

The University of Toronto,
Chemical Laboratory,
March, 1908.

SOME CUPROUS AMMONIA HALIDES

BY STEWART J. LLOYD

The work described in the following pages consists essentially in the determination of the compounds existing between the cuprous halides and ammonia within the temperature range of zero and 150° and in the measurement of their temperature pressure curves. With one exception no records of any cuprous-halide ammonia compounds exist, although the analogous silver compounds were among the first to be investigated. The exception referred to is a description by Ritthauser[1] of a compound $Cu_4Cl_4 2NH_3$ which he obtained by dissolving copper filings in aqueous ammonium chloride. This compound I was unable to obtain either by his or any other method, and in view of the extreme readiness with which similar substances absorb water its formation from aqueous solution seems improbable. As the existence of cuprous fluoride appears to be in doubt no attempt was made to prepare compounds of it.

The method of investigation employed was the usual one. The cuprous halide under examination was saturated with ammonia gas at zero, and its vapor pressure at some constant temperature observed as ammonia was gradually withdrawn from it. By plotting the molecular amounts of ammonia remaining against the pressure observed, curves were obtained which indicate clearly the number and composition of the compounds formed. To measure the temperature pressure curve of any particular compound, then, it was necessary merely to keep withdrawing ammonia at the constant temperature until the desired section of the curve had been reached, and then to vary the temperature and read the corresponding pressures.

The compounds containing the largest quantities of ammonia were prepared by passing thoroughly dried ammonia

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[1] J. Pr. Chem., 59, 369.

gas over small quantities of the salts contained in bent tubes which were immersed in a freezing mixture. It was found necessary to take unusual precautions to dry the ammonia, and it was passed through two three-foot tubes filled with lime, as well as four towers of the same material. It is necessary also to pass the ammonia very slowly over the halides, as the heat of reaction is considerable and sometimes the compound fuses and is quite useless for pressure measurements. All the compounds observed absorbed moisture very readily from the air, taking up a considerable amount even upon transference from one vessel to another.

The apparatus used in the measurements consisted of a mercury air pump and a manometer, to which was connected a small glass cell 5 cm long and 1 cm in diameter which contained the compound under examination. About 5 grams of the substance were used at a time. For temperatures up to 70° C. a water bath was used; for higher temperatures an oil bath. An Ostwald thermo-regulator enabled the temperature to be kept constant to within two-tenths of a degree.

Within the range of temperature mentioned, cuprous iodide and cuprous bromide each form two compounds with ammonia; cuprous chloride, however, forms three. The formula of each, together with its color and approximate melting point, is given below.

		M. P.
$Cu_2I_2\ 6NH_3$	Light green	105
$Cu_2I_2\ 3NH_3$	Dark brown	117
$Cu_2Br_2\ 6NH_3$	Green	115
$Cu_2Br_2\ 3NH_3$	Brown	135
$Cu_2Cl_2\ 6NH_3$	Green	123
$Cu_2Cl_2\ 3NH_3$	Light brown	144
$Cu_2Cl_2\ NH_3$	Dark brown	162

Tables 1, 2 and 3 give the pressures in mm of mercury at certain temperatures shown by each of the three halides, as ammonia gas was gradually removed. The results are shown graphically in Figs. 1, 2 and 3.

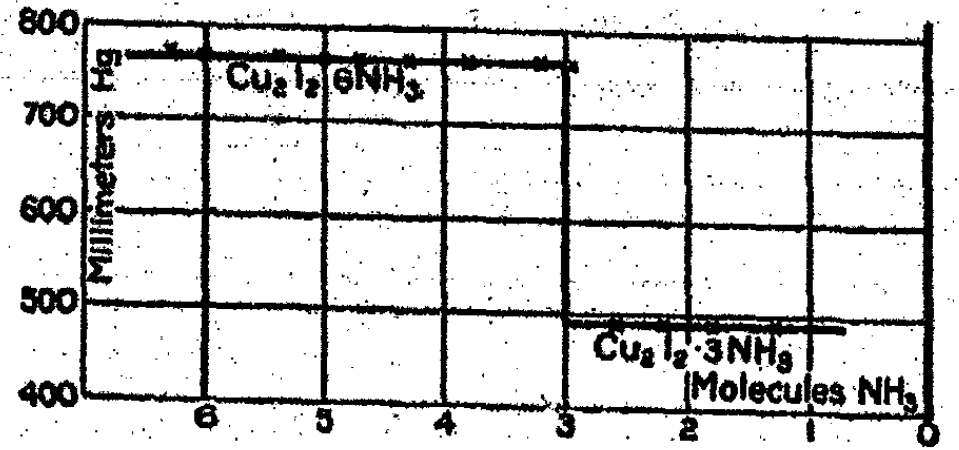

Fig. 1

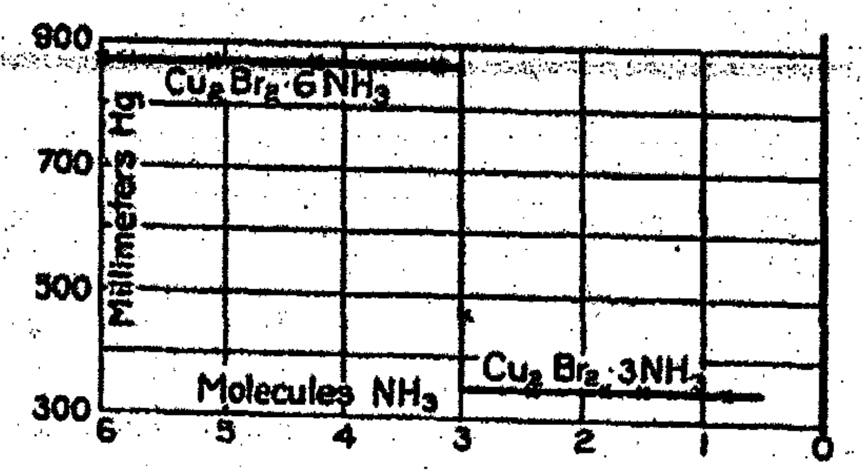

Fig. 2

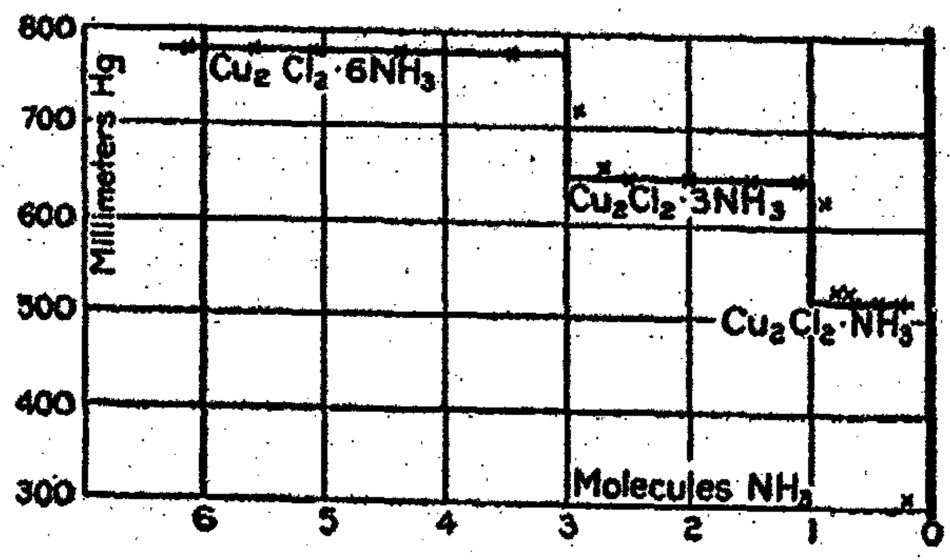

Fig. 3

TABLE I

$Cu_2I_2(NH_3)_x$ Temp. 51.75°

Mols (NH_3)	Pressure.
6.25	771
6.1	768
5.8	766
5.4	767
5.0	768
4.7	765
4.3	767
3.8	769
3.2	768
2.95	767
....	...
2.6	491
2.2	489
1.8	490
1.3	487
0.8	489
0.5	490
0.35	180
0.2	90

TABLE II

$Cu_2Br_2(NH_3)_x$ Temp. 100° C.

Mols (NH_3)	Pressure.
6.0	867
5.1	865
4.2	867
3.2	868
....	...
2.95	472
2.4	360
1.8	352
1.5	353
0.75	352
0.5	100
0.25	62

TABLE III

$Cu_2Cl_2(NH_3)_x$ Temp. 90° C.

Mols (NH_3)	Pressure.
6.1	783
5.6	780
5.1	779
4.4	781
3.4	778
....	...
2.9	720
2.7	660
2.5	650
2.0	651
1.5	648
1.1	649
....	...
0.9	620
0.8	530
0.65	522
0.45	523
0.3	522
0.2	312
0.1	40

The following tables contain the pressure temperature curves of the seven compounds.

$Cu_2I_26NH_3$		$Cu_2I_23NH_3$	
Temp.	Pressure.	Temp.	Pressure.
18.25	150	17.5	60
38.5	422	20.25	75
47.0	615	41.0	272
52.0	784	45.0	330
56.0	952	48.0	396
58.75	1084	51.75	490
		59.5	742
		65.0	999

$Cu_2Br_2(6NH_3)$

Temp.	Pressure.
69.0	214
78.5	347
90.5	601
100.0	865

$Cu_2Br_2(3NH_3)$

Temp.	Pressure.
83	200
100	352
110	456
120	620

$Cu_2Cl_2(6NH_3)$

Temp.	Pressure.
88	736
93	915
98	1132
110	1650

$Cu_2Cl_23NH_3$

Temp.	Pressure.
67.5	324
85.0	567
92.0	700
100.0	845

$Cu_2Cl_2NH_3$

Temp.	Pressure.
87.0	518
90.0	523
120.0	680
135.5	819

This work was undertaken at the suggestion of Dr. J. W. Walker of McGill University, to whom the writer wishes to express his thanks.

NOTE ON PROFESSOR J. E. TREVOR'S PAPER ON OSMOTIC PRESSURE

BY ALFRED W. PORTER, B.SC.[1]

The paper of Professor Trevor in the March number of this Journal is of great interest to me as it is of great value to have a question looked at from several points of view. I was aware that my equation was deducible by Gibbs's method. The much greater elegance of such a deduction is, however, compensated by the fact that the abstract nature of the proof prevents a complete realization of the argument except by a special few who have grown fully familar with Gibbs's work. The method adopted by me in my published paper is one which, though considerably longer, is easily understandable by any one acquainted with the Principle of Work. Soon after the publication of my paper I realized that the proof, while still depending upon the consideration of the same cycle, could be very much abridged. For since in any stage of the cycle

$$\int_1^2 pdv = p_2v_2 - p_1v_1 - \int_1^2 vdp\ ;$$

and since the total change in pv during the whole cycle must be nothing, it follows that not only is

$$\sum\int pdv = 0 \quad \text{but also} \quad \sum\int vdp = 0$$

for the cyclic transformation. If the value of this quantity is obtained for each stage the sum of the terms gives my equation *without further reduction*; it can therefore be written down at once. The relation to the method of Gibbs is obvious; but to each individual understanding the thermodynamic potential probably a thousand could be found who would understand the proof just outlined.

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[1] Fellow of and Assistant Professor of Physics in University of London (University College), England.

The cyclic method can be adapted to deal with the question of the heat of dilution by considering a cycle, parts of which take place at different temperatures. The easiest method of finding the expression for the dissipation of dilution is to observe that if instead of mixing the solute with the solution through the osmotic membrane it be desired to mix it irreversibly it is necessary to first raise its pressure from $p - \mathrm{P}$ to p; this operation introduces the *additional* term

$$\int_{p-\mathrm{P}}^{p} v_s dp$$

into the equation, while the other terms remain unchanged. On the other hand, the total heat changes during this cycle differ in this case from the reversible case simply by the dissipation of dilution, which can therefore be equated to

$$\int_{p-\mathrm{P}}^{p} v_s dp.$$

I wish further to add that the equation toward the lower half of p. 148 giving the rate of change of osmotic pressure with concentration can be obtained at once by the differentiation of my equation (1); but a very much simpler equation can be obtained by differentiating my equation (12). This simpler equation is

$$v_s(p - \mathrm{P}, \theta) \frac{\partial \mathrm{P}}{\partial m_1} = - v_a(p_1 \theta) \frac{\partial p_1}{\partial m_1} (p, m_1, \theta)$$

where the notation is modelled on Professor Trevor's. Here $p_1(p, m_1, \theta)$ is the vapor pressure of the solution when the latter is under the hydrostatic pressure p; and the differentiation is to be performed at constant pressure and temperature. In my notation this equation is written

$$u_{p_0} \frac{\partial \mathrm{P}}{\partial m_1} = - v_{\pi_p} \frac{\partial \pi_p}{\partial m_1}.$$

POTENTIAL OF A HYDROGEN ELECTRODE IN ACID AND ALKALINE SOLUTIONS

C. L. A. SCHMIDT AND C. P. FINGER

(From the Laboratory of Physical Chemistry, University of California.)

A number of different methods have been proposed for the preparation of solutions containing a definite concentration of H' ions. In determining small concentrations of H or OH ions colorimetrically by means of indicators, it at once becomes evident that the standard solutions must be prepared with considerable accuracy and at the same time of such substances as may be prepared in a high state of purity.

Friedenthal[1] prepared a scale of H' concentrations varying from 2nH' to 5×10^{-15} H' using strong acids and bases at various dilutions. He was then able to determine the colors which various indicators gave in his solutions of known H' concentration. It was suggested by Von-Szily that solutions near the neutral point might be easily prepared by using mixtures of N/10 NaH_2PO_4, which reacts weakly acid, and N/10 Na_2HPO_4, which reacts weakly alkaline. Measurement of the H' concentration in these solutions was carried out by E. Salm.

Salesky and Fels[2] showed that by using mixtures of ammonia and ammonium chloride or acetic acid and sodium acetate, solutions of definite H'-concentrations could be prepared with a high degree of accuracy.

The work begun by Friedenthal was further extended by E. Salm.[3] He determined by the gas chain method the exact H' concentration in the solutions forming the Von-Szily scale of acid and alkaline phosphates. Knowing the

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[1] Friedenthal: Zeit. Electrochemie, 10, 113–119 (1904).

[2] Salesky and Fels: Ibid., 10, 204–214 (1904).

[3] Salm: Ibid., 10, 341–346 (1904).

$H^{\cdot}$-concentration of a number of these solutions, it was easy to prepare other solutions near the neutral point having definite $H^{\cdot}$ concentrations. In a subsequent work, Salm,[1] by electromotive force measurements, determined the $H^{\cdot}$ concentrations in all the solutions used in making up the ionic-H scale, thus bringing together his own earlier work on the phosphate scale, and that of Friedenthal. His table giving the colors of indicators in solutions of known $H^{\cdot}$ concentration is the most complete on the subject we now have. By the use of indicators, not only can the $H^{\cdot}$ concentration in a solution be determined, but as Salm has shown,[2] the dissociation constants of acids, bases, and even indicators may be determined colorimetrically.

Experimental

As has been shown by previous workers, it is easier and more accurate to prepare solutions of definite $H^{\cdot}$ concentration near the neutral point by using a weak acid combined with a strong base or a strong acid combined with a weak base rather than a strong acid or base at high dilutions. For this reason such substances as sodium phosphate, sodium acetate, and ammonium chloride have previously been used.

In the present work boric acid and the various borates of sodium were used in making a scale of varying $H^{\cdot}$ concentrations. At the suggestion of Professor Cottrell, the work was begun by one of us (Finger) in August 1906, but was not completed. During the last semester the work was independently repeated (Schmidt) and the whole completed by carrying the alkaline scale up to Na_3BO_3. The data on the solutions from H_3BO_3 to NaH_2BO_3 were thus checked by two independent series of observations.

The method pursued in obtaining the data was as follows: Standard solutions of H_3BO_3, $Na_2B_4O_7$, NaH_2BO_3, Na_2HBO_3, and Na_3BO_3, were prepared, each containing 0.25 gram atom of boron per liter, and the potential of a hydrogen electrode

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[1] Salm: Zeit. phys. Chem., 57, 471 (1906).

[2] Salm: Ibid., 57, 471 (1906); Zeit. Electrochemie, 12, 99 (1906).

immersed in these solutions determined by the potentiometer method, using a N/10 calomel electrode as the other half of the cell. Mixtures of the above solutions, as shown in the tabulated scheme, were also made, and the potential in each of them likewise determined. This gave a series of solutions, each having a definite $H^{\cdot}$ concentration, the whole forming a scale, varying from a weak acid on the one side, through the neutral point, to a strong base on the other.

The various solutions used were made as follows:

(1) A solution of $M/4H_3BO_3$. The boric acid was recrystallized from Kahlbaum's boric acid and dried at 50° C.

(2) A solution of $M/16$ $Na_2B_4O_7$. The borax was recrystallized and dried in contact with air, the crystalline borax, $Na_2B_4O_7.10H_2O$, being obtained.

(3) A solution of $M/4$ NaH_2BO_3. This was prepared by dissolving 23.89 grams of $Na_2B_4O_7.10H_2O$ in water, adding 63.8 cc of 1.959 N NaOH and enough water to make a liter. The increased step in alkalinity can be represented by the equation:

$$Na_2B_4O_7 + 2NaOH + 3H_2O = 4NaH_2BO_3.$$

(4) A solution of $M/4$ Na_2HBO_3. The solution was made in the same manner as the previous one except that three times as much NaOH or 191.4 cc were added. We can represent the formation of this compound by the equation:

$$Na_2B_4O_7 + 6\,NaOH = 4\,Na_2HBO_3 + 3H_2O.$$

(5) A solution of Na_3BO_3, also $M/4$. The liter of solution contained 23.89 grams of $Na_2B_4O_7.10H_2O$ and 319 cc or 1.959 N NaOH. The formation of this compound can be represented:

$$Na_2B_4O_7 + 10\,NaOH = 4\,Na_3BO_3 + 5H_2O.$$

All of the above solutions contain 0.25 gram atom of boron per liter. The NaOH solution was kept for some time over $Ca(OH)_2$ to insure an absence of carbonates. It was standardized against succinic acid (twice recrystallized and dried over H_2SO_4), phenolphthalein being used as indicator.

The general arrangement of the apparatus is shown in Figs. 1 and 2. The electromotive force was measured on a 100 cm potentiometer wire. Current was supplied by a storage battery, which was checked against a Weston cell just after each final reading with the gas cell. To detect the zero point on the bridge a sensitive d'Arsonval galvanometer was used. The resistance in the boric acid solution was so high that with a less sensitive instrument a satisfactory read-

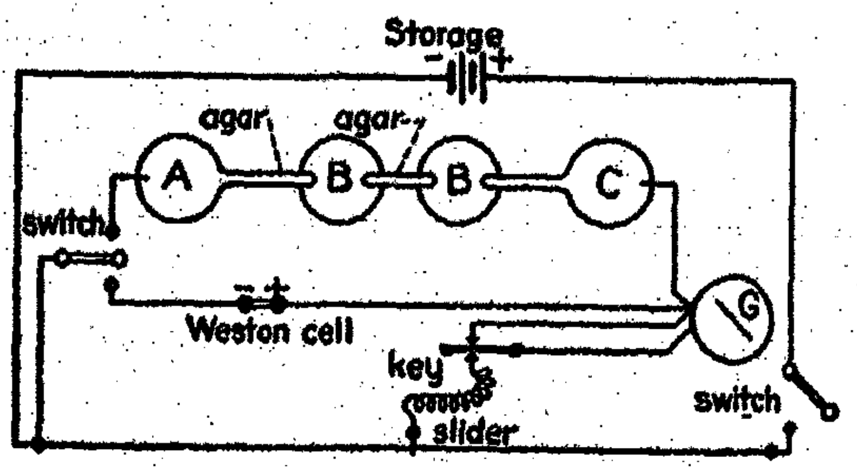

Fig. 1

A = Hydrogen gas cell.
B = Beaker with N/10 KCl.
C = N/10 KCl-Hg-calomel-electrode.
D = Galvanometer.

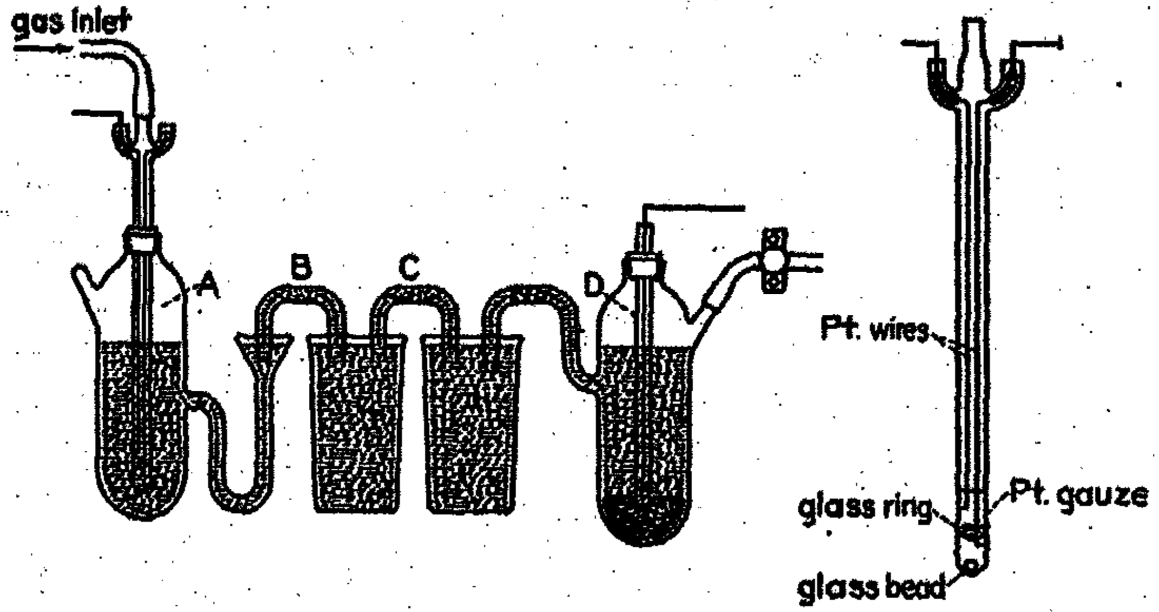

Fig. 2

A = Cell holding borate solution.
B = Agar tube saturated with KCl.
C = Agar tube containing N/10 KCl.
D = Normal calomel electrode.

ing could not be obtained. On repeating measurements with the same solution, the bridge readings agreed within 1 mm. On repeating the measurement with a new solution, the bridge readings did not vary more than 2 mm from the former reading.

The cell containing the borate solution is shown in Fig. 2. The side cup has the advantage over the type usually used in that there is less danger of contaminating the solution in the cell, by the siphoning of one solution over into the other. The side tube is connected with the beaker containing the N/10 KCl by a tube filled with agar-agar jelly, which had been made up in a saturated solution of KCl. This reduces to a minimum any back electromotive force due to contact of the two solutions.[1]

The standard electrode used was the calomel electrode made up of Hg.-HgCl-N/10 KCl. Contact between the gas electrode and the calomel electrode was made through two small beakers filled with N/10 KCl, the latter being connected by a gelatinized agar-agar tube prepared in a solution of N/10 KCl. The hydrogen electrode was of a design due to Professor Cottrell, which has been much used in this laboratory.[2] It is also shown in Fig. 2. On the end of a glass tube were sealed two cylinders of platinum gauze, the two being separated by fusing them into a ring of glass (*a*). Two separate platinum wires, welded respectively to the two gauzes, led from each of these two sections up through the tube, connecting with two mercury cups. The gauze was so fine that the cylinders were completely filled with gas before it could escape through the meshes and bubble up through the liquid. In this way the three phases, gas, liquid and solid, are brought into the most intimate contact and equilibrium is quickly established. By interchanging the connection in the mercury cups, two readings are obtained, this serving as a check. The gauze cylinders were frequently replatinized with Lummer and Kurlbaum's solution.

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[1] Bjerrum: Zeit. phys. Chem., 53, 428–440 (1905).
[2] See also Robertson: Jour. phys. Chem., 11, 442 (1907).

The hydrogen gas was obtained by electrolysis of dilute sulphuric acid in the apparatus shown in Fig. 3. The latter consisted of an outer cylindrical glass containing vessel (*a*), down the center of which passed a wide glass tube (*b*) having a porous earthenware extension (*c*) cemented into its lower end. Inside of the latter was the negative electrode (*d*) of sheet platinum sealed into a glass tube, connection being made through mercury in the usual manner. The positive electrode (*e*) was another sheet of platinum wrapped about the outside of the porous cylinder. Current was supplied from a storage battery of ten volts; the cells being charged when necessary without interrupting the generator. By means of a pinch-cock, the current of hydrogen from the generator can be regulated, at the same time a very uniform pressure being obtained. The generator can be left running for several days, without any attention being given to it.

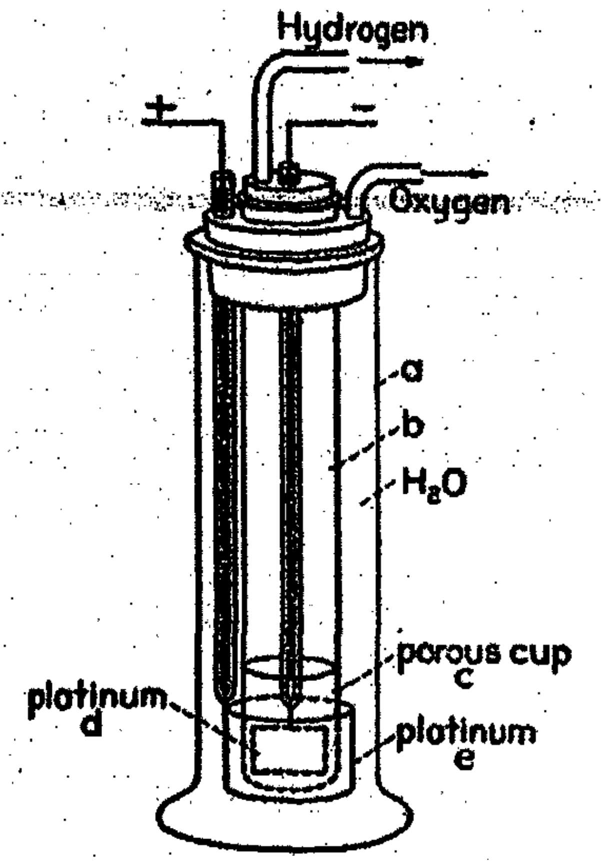

Fig. 3

To take out any oxygen or hydrogen peroxide which might have come over from the generator, the gas was passed through a glass tube, loosely filled with platinized asbestos, and having a coil of fine resistance wire wrapped around it, so that when a current of 1/2 ampere was passed through the coil the gas was heated to further insure complete catalysis and thus rid it of any oxygen.

The hydrogen was allowed to bubble through the solution at a slow rate for an hour or more and a reading then taken. If after fifteen minutes the reading was constant and equal on both sections of the electrodes, readings being taken by interchanging the connections in the mercury cups, equilibrium was assumed to be established. In order to insure equilibrium in solutions near the neutral point, the gas was allowed to bubble through the solution over night and readings taken the next morning. The variation due to a few degrees shift in temperature was found to be within the limits of experimental error. The temperature of the laboratory did not vary more than 5° C. The results are given in tabulated form (Table 1). For the sake of completeness, the

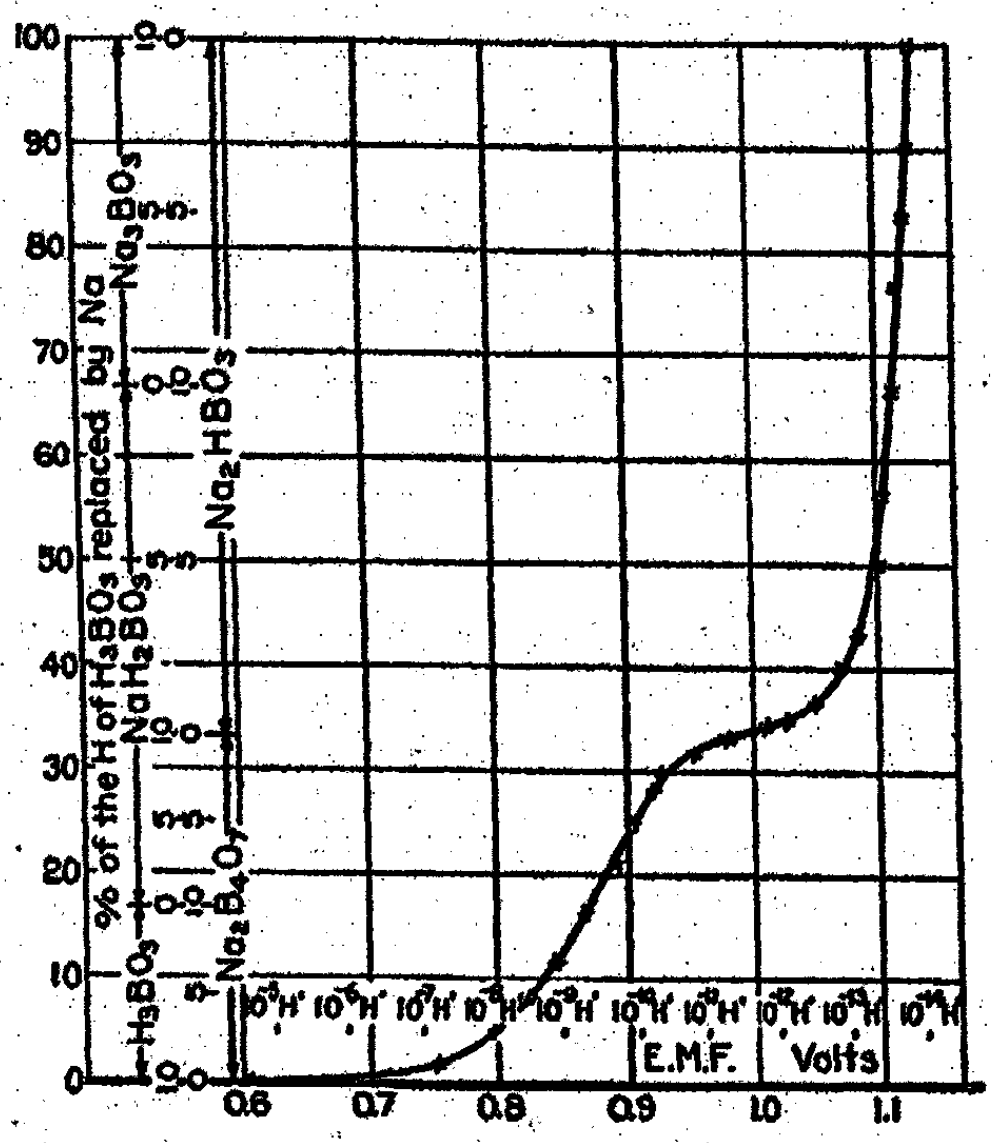

Fig. 4

temperatures at which readings were taken are also given. Plotting electromotive force as abscissae and the percentage of the hydrogen of the H_3BO_3 replaced by Na (increase of basicity of the mixtures) as ordinates, gives the curve shown in Fig. 4.

TABLE I

Data.

a = Parts by volume of solutions used.
b = Bridge readings with gas cell.
c = Bridge readings with standard cell.
E = E. M. F. of each mixture in volts.
t = Temperatures at which readings were taken.
e = % of H of H_3BO_3 replaced by Na.

(*a*)		(*b*)	(*c*)	(E)	(*t*)	(*e*)
H_3BO_3	$Na_2B_4O_7$					
10	0	32.41	54.53	0.605	16.8°C.	0.0
9	1	40.75	55.10	0.753	15.0	1.67
7	3	42.09	53.69	0.798	15.8	5.00
5	5	43.49	53.51	0.828	20.8	8.33
3	7	44.58	53.64	0.847	16.0	11.67
0	10	46.49	54.50	0.869	15.7	16.67
NaH_2BO_3						
3	7	47.03	53.72	0.893	17.9	21.67
5	5	47.77	53.71	0.906	15.9	25.00
7	3	48.60	53.72	0.922	16.6	28.33
8	2	49.46	54.22	0.929	16.4	30.00
9	1	51.25	54.58	0.957	15.2	31.67
10	0	51.74	53.72	0.981	15.8	33.33
	Na_2HBO_3					
9.5	0.5	52.25	51.78	1.028	15.0	35.00
9	1	53.48	51.78	1.052	15.1	36.67
8	2	54.25	51.78	1.067	15.0	40.00
7	3	57.32	53.81	1.085	15.3	43.33
5	5	58.05	53.83	1.099	16.0	50.00
3	7	58.45	53.90	1.105	16.0	56.67
0	10	58.85	53.81	1.114	15.4	66.67
Na_3BO_3						
3	7	59.17	53.98	1.117	16.7	76.67
5	5	59.36	53.98	1.122	16.7	83.34
7	3	59.93	54.22	1.126	16.8	90.00
10	0	59.75	53.90	1.129	16.6	100.00

To determine the neutral point on the curve Nernst's formula is used:

$$\pi = \frac{1.99\ T \times 10^{-4}}{n} \log. \frac{C_1}{C_2}$$

Assuming 16° C as the average temperature of these measurements, and the $H^{\cdot}$-concentration of pure water[1] at this temperature as 0.75×10^{-7}, the difference of potential of a hydrogen electrode immersed respectively in a solution of $\frac{N}{1}$ H-ion concentration and in pure water becomes

$$\pi = 0.0575 \log. \frac{1}{0.75 \times 10^{-7}}$$
$$= 0.410$$

The difference of potential between the hydrogen electrode in a N/1 H-solution and the $\frac{N}{10}$ calomel electrode to which the electromotive force of the table and curve refer, is 0.336 volt.[2] [3] Adding this to the value of (0.336 + 0.410) we get 0.746 volt for the neutral point. For a $H^{\cdot}$ concentration of 10^{-7} the corresponding voltage is 0.739. For a $H^{\cdot}$ concentration of 10^{-6}, 0.0575 volt is subtracted or for a $H^{\cdot}$ concentration of 10^{-8} it is added, this being the change in voltage for a tenfold change in H concentration. In a similar manner the $H^{\cdot}$-concentration corresponding to any other electromotive force can be found on the curve.

The present scale to a certain extent runs parallel to the scales already worked out and so can be used as a check. Boric acid and borax may be readily obtained in a very pure state, this making it easy to duplicate results at any time.

An interesting fact is shown by the curve, namely, the existence in solution of the compound NaH_2BO_3 or the anhydride $NaBO_2$ or the corresponding ions H_2BO_3 and BO_2. The curve shows also that borax, $Na_2B_4O_7$, even though it is ob-

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[1] The $H^{\cdot}$-concentration for water at 16° C is taken as $.75 \times 10^{-7}$. Nernst, Zeit. phys. Chem., gives 0.8×10^{-7} at 18° C.

[2] Richards: Zeit. phys. Chem., 24, 37 (1897).

[3] Ostwald-Luther: Physico-Chemische Messung, pp. 384 (1902).

tained as a crystalline compound, does not to any appreciable extent exist in solution, for if it did, we would have a flat portion on the curve corresponding to the compound. The fact that the flat portion corresponds to NaH_2BO_3 or $NaBO_2$ shows that these compounds or the corresponding ions H_2BO_3 and BO_2 exist in solution.

The existence of the compound having the composition KBO_2 or KH_2BO_3 was shown by Noyes and Whitney.[1] Varying amounts of boric acid were added to a solution of KOH and the freezing point of the mixture determined. There was no material lowering of the freezing point by adding small quantities of H_3BO_3 until one molecule of boric acid had been added for each molecule of KOH. The addition of more boric acid increases the freezing point of the solution, thus showing that the number of molecules is not changed by the addition of boric acid up to equal molecular ratio. Noyes and Whitney further point out that the results agree with the thermochemical measurements of Thomsen.

Kahlenberg and Schreiner[2] by making further determinations of the freezing point in sodium borate solutions, and also by conductivity measurements, came to the conclusion that the compound NaH_2BO_3 was formed. Shelton,[3] by measuring the conductivity in solutions made by adding varying quantities of the solution ($NaOH + 4H_3BO_3$) to a definite quantity of NaOH solution, has confirmed the results of Kahlenberg and Schreiner. He, however, regards the formation of $NaBO_2$ as being the more probable for the reason that silver métaborate, $AgBO_2$, is formed when silver nitrate is added to a solution of borax. It is interesting to note that the compound $NaBO_2$ has been known for some time. Benedict[4] obtained the crystalline substances $NaBO_2.4H_2O$ and $NaBO_2.H_2O$ from solutions of borax to which NaOH had

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[1] Noyes and Whitney: Zeit. phys. Chem., 15, 694–698 (1894).

[2] Kahlenberg and Schreiner: Zeit. phys. Chem., 20, 547–568 (1896).

[3] Shelton: Zeit. phys. Chem., 43, 494–498 (1903).

[4] Benedikt: Ber. chem. Ges. Berlin, 7, 703

been added. The compound $NaBO_2$ was also known to Berzelius.

Conclusions

(1) This work corroborates the results previously obtained by other workers showing that the compound NaH_2BO_3, $NaBO_2$, or a mixture of the two are the only ones formed in solution to any appreciable extent on mixing H_3BO_3 and NaOH. As to which or to what proportion of each of the above really exist in solution and to what extent they are dissociated into Na, H_2BO_3 and BO_2, the present work gives no clew.

(2) By determining the $H^{\cdot}$ concentration in a number of mixtures of NaOH and H_3BO_3 solutions, each containing 0.25 gram atom of boron per liter, a series of readily reproducible standards for the colorimetric determination of acids and bases have been provided.

In conclusion we wish to thank Professor F. G. Cottrell for the suggestion of this problem and for the constant interest he has taken in the work, and Professor T. Brailsford Robertson for his friendly criticisms.

THE ELECTROCHEMISTRY OF LIGHT. III

BY WILDER D. BANCROFT

Halogen Carriers

Sunlight causes chlorine or bromine to react with toluene; ferric chloride has a similar effect; and substitution products are also obtained by the action of the current on a mixture of toluene and aqueous hydrochloric acid. Under the influence of sunlight ferric chloride reacts with alcohol, though slowly. Since some halogen carriers act in the same way as sunlight, while others act differently, it will simplify matters to consider the whole question of halogen carriers. The facts are not on record in any single book or article on organic chemistry, so far as I can learn. We will, therefore, take up the experimental data first and will afterwards consider whether any theory can be devised that will fit them all.

In the dark, benzene does not react with chlorine at any temperature up to the boiling point of the solution under atmospheric pressure.[1] It is usually stated that chlorine reacts with boiling benzene in the dark but the experiments of Slator[2] and of Goldberg[3] prove that this is really a photochemical reaction and that it does not take place if no light reaches the boiling benzene. In bright sunlight benzene hexachloride[4] is formed when benzene and chlorine are brought together even at 0°. With rising temperature the reaction takes place more readily until, at the boiling point, it takes place unless light is rigidly excluded. Benzene hexachloride is also obtained when chlorine is bubbled into a mixture of benzene with water or dilute caustic soda.[5] Neither light nor

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[1] Willgerodt: Jour. prakt. Chemie [2], 34, 264 (1886).

[2] Zeit. phys. Chem., 45, 513 (1903).

[3] Zeit. wiss. Photographie, 4, 61 (1906).

[4] In this paper it is not necessary to distinguish between the α- and the β-hexachlorides.

[5] Matthews: Jour. Chem. Soc., 59, 165 (1891); 61, 103 (1892). Goldberg: Zeit. wiss. Photographie, 4, 63 (1904).

high temperature is necessary for this reaction. Chlorine reacts with benzene in presence of phosphorus pentachloride[1] producing the hexachloride. In this reaction the phosphorus pentachloride plays the part of a carrier. When benzene, chlorine and iodine monochloride are mixed in the dark, some hexachloride is formed,[2] though most of the chlorine reacts to form substitution products. In presence of ferric chloride,[3] stannic chloride,[4] aluminum chloride,[5] antimony pentachloride,[6] molybdenum pentachloride,[7] sulphur,[8] sulphuryl chloride,[9] or sulphuric acid,[10] chlorine and benzene react, forming substitution products only. With iodine monochloride alone the reaction takes place very slowly in the dark and yields substitution products exclusively in the light.[11]

Benzene and bromine react slowly in the dark, forming brombenzene and hydrobromic acid. This reaction does not run to an end. When the benzene and the bromine are present in equivalent quantities, only fifty percent of the benzene is converted into brombenzene.[12] No experiments have been made to determine whether the brombenzene or the hydrobromic acid is the disturbing factor in this case, but Bruner's work[13] makes it probable that the formation of HBr_3 is the cause of the phenomenon. The fact that bromine acts on benzene in the dark, while chlorine is said not to, is not due to the greater reacting power of ben-

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[1] Willgerodt: Jour. prakt. Chem. [2], 34, 264 (1886).

[2] Müller: Jour. Chem. Soc., 15, 41 (1862); Slator: Zeit. phys. Chem., 45, 524 (1903).

[3] Page: Liebig's Ann., 225, 196 (1884).

[4] Pétricou: Bull. Soc. chim. Paris [3], 3, 189 (1890).

[5] Gustavson: Ber. chem. Ges. Berlin, 10, 911 (1877).

[6] Beilstein and Kurbatow: Ber. chem. Ges. Berlin, 8, 1417 (1875).

[7] Aronheim: Ibid., 8, 1400 (1875).

[8] Willgerodt: Jour. prakt. Chem. [2], 34, 264 (1886).

[9] Dubois: Zeit. Chemie [2], 2, 705.

[10] Istrati and Pétricou: Bull. Soc. chim. Paris [3], 5, 165 (1891).

[11] Slator: Zeit. phys. Chem., 45, 532 (1903).

[12] Schramm: Ber. chem. Ges. Berlin, 18, 350 (1885).

[13] Zeit. phys. Chem., 41, 513 (1902).

zene but to its greater solubility in benzene. A dilute solution of bromine in benzene remains practically unchanged.[1]

In sunlight, bromine and benzene form benzene hexabromide.[2] Hexabromide is also formed, together with some substitution products, when bromine is added to a mixture of benzene and water or dilute aqueous caustic soda solution,[3] preferably in the sunlight though this is not absolutely necessary. In presence of iodine, ferric bromide, etc., bromine substitution products are obtained. Ferric chloride also acts as a bromine carrier,[4] hydrochloric acid being evolved until the ferric chloride has been converted completely into ferric bromide.

Very little of an accurate nature is known in regard to the halogen addition products of toluene and we do not need to consider them. With toluene we have the contrast between substitution in the benzene ring and substitution in the methyl group or side chain instead of the contrast between the substitution products and the addition products in the case of benzene.

Substitution in the side chain takes place when chlorine and toluene at 0° are exposed to sunlight[5] and when chlorine is led into boiling toluene.[6] It is probable that the latter method of preparation is a photochemical one, but there is no direct evidence on the point. Phosphorus pentachloride acts as a chlorine carrier with toluene, forming benzyl chloride.[7] Side-chain substitution occurs with nitrotoluene when sulphur is used as a carrier.[8] I could not find any record of any one having bubbled chlorine through an emulsion of toluene and dilute aqueous caustic soda, as Matthews did

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[1] Bruner: Zeit. phys. Chem., 41, 513 (1902).

[2] Mitscherlich: Pogg. Ann., 35, 374 (1835).

[3] Matthews: Jour. Chem. Soc., 59, 165 (1891); 61, 103 (1892); 73, 243 (1898). Orndorff and Howells: Am. Chem. Jour., 18, 312 (1896).

[4] Scheufelen: Liebig's Ann., 231, 152 (1885).

[5] Schramm: Ber. chem. Ges. Berlin, 18, 606 (1885).

[6] Cannizzaro: Comptes rendus, 41, 517 (1855).

[7] Colson and Gautier: Ann. Chim. Phys. [6], 11, 19 (1887).

[8] Häussermann and Beck: Ber. chem. Ges. Berlin, 25, 2445 (1892).

with benzene. Some experiments by Mr. Schluederberg in my laboratory have shown that the substitution takes place both in the ring and in the side chain.

Chlorine probably reacts slowly with toluene in the dark, substituting mostly in the ring; but Seelig's statements[1] are very vague and one does not know what to make of the remark that addition products are formed at 80°. Such carriers as $FeCl_3$, $MoCl_5$, $SbCl_5$, and ICl substitute exclusively in the ring under ordinary circumstances. The statement is even made that with iodine and boiling toluene no benzyl chloride is formed.[2] In view of the results obtained for the action of bromine on boiling toluene in presence of IBr, it is safe to assume that this sweeping statement is true only so long as the iodine content of the solution does not fall below a certain minimum.

Bruner[3] finds that toluene and bromine react in the dark with substitution both in the ring and in the side chain, while Schramm[4] reports that only ring substitution takes place. This discrepancy is due chiefly to a difference in the conditions of the experiments. Schramm worked with toluene and bromine in equivalent quantities while Bruner studied the behavior of dilute solutions of bromine in toluene. The effect of concentration is shown in Table I, compiled from Bruner's data.

TABLE I

Temperature 25°

Concentration.	Percent $C_6H_5CH_2Br$	Concentration	Percent $C_6H_5CH_2Br$
$1Br_2 + 5C_7H_8$	2.7	$1Br_2 + 25C_7H_8$	36.3
$1Br_2 + 10C_7H_8$	10.4	$1Br_2 + 40C_7H_8$	45.6
$1Br_2 + 15C_7H_8$	24.4	$1Br_2 + 100C_7H_8$	42.4

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[1] Liebig's Ann., 237, 169 (1887).

[2] Beilstein and Geitner: Liebig's Ann., 139, 331 (1866).

[3] Bull. Acad. Sci. Cracovie, 1907, 693.

[4] Schramm: Ber. chem. Ges. Berlin, 18, 350 (1885).

With rising temperature, relatively more benzyl bromide is formed as is shown in Table II, which is also compiled from Bruner's data.

TABLE II

$1Br_2 + 40C_7H_8$

Temp.	Percent $C_6H_5CH_2Br$	Temp.	Percent $C_6H_5CH_2Br$
0°	8.7	45°	87.0
10	18.0	58.5	94.1
25	45.6	74	99.5
35	974.0		

In these experiments the toluene and bromine were in sealed glass tubes enclosed in a metal casing. They were thus protected entirely from the light. In the experiments at the higher temperatures, some reaction undoubtedly took place while the tubes were heating and the percentages of benzyl bromide, as given in Table II, are undoubtedly a little low at the higher temperatures. Since these experiments were undertaken chiefly as a study in chemical kinetics, they were not carried through to an end and the data in the two tables refer to the percentages of benzyl bromide formed at the end of the run when 90–95 percent of the bromine had been used up. While the data do not therefore represent the percentages when the reaction has come to an end, the general relations remain the same.

Some experiments were made by Bruner with carbon tetrachloride as solvent. This solvent had no effect on the relative reaction velocities, the percentages of benzyl bromide being practically the same whether the reaction took place in presence or in absence of carbon tetrachloride. Very different results were obtained with nitrobenzene as solvent. A mixture was made up containing 75 parts nitrobenzene and 25 parts toluene by volume. One gram of bromine was added to 26.6 cc. of the mixture. The results are given in Table III. The effect of the nitrobenzene is very marked.

TABLE III
75 Vol Percent $C_6H_5NO_2$ + 25 Vol Percent C_7H_8
1 g Br_2 to 26.4 cc solution

Temp.	Percent $C_6H_5CH_2Br$	Temp.	Percent $C_6H_5CH_2Br$
25°	1.3	45°	11.4
35	2.9	74	18.9

Very little benzyl bromide is formed below 40° and even at 74° there is only 19 percent as against 100 percent when no nitrobenzene is present.

In sunlight, benzyl bromide is the sole product even at zero and in concentrated solutions.[1] With ferric bromide or ferric chloride as carrier, ring substitution is the only one. With iodine monobrombromide as carrier, ring substitution is usually the only reaction. Jackson and Field[2] have shown that at higher temperatures benzylbromide is formed even in presence of iodine, the relative amount of benzyl bromide increasing with decreasing concentration of iodine. This has been studied in more detail by Bruner.[3] The results are tabulated in Table IV. The first column contains the molecular percentage of iodine to bromine. In the remaining columns are given the percentages of benzyl bromide at the different temperatures.

TABLE IV
$1 Br_2 + 40 C_7H_8$
Percent $C_6H_5CH_2Br$

Percent I/Br	0	25°	35°	45°
1.0	0.0	29.5	41.0	67.0
2.5	—	10.3	18.1	38.1
5.0	0.0	4.0		
10.0	0.0	1.2		

The reaction velocity experiments showed that the ring substitution and the chain substitution were independent

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[1] Schramm: Ber., 18 (1885).
[2] Am. Chem. Jour., 2, 10 (1881).
[3] Bull. Acad. Sci. Cracovie, 1907, 710.

reactions and that the iodine did not change the rate of the latter reaction. According to Schramm,[1] bromtoluene alone is formed when the solution containing iodine is exposed to direct sunlight. From Bruner's experiments it is safe to conclude that Schramm's statement applies only to the conditions under which he worked. With dilute solutions of bromine in benzene and with decreasing concentration of iodine the relative yield of benzyl bromide must increase. As Table IV shows, nearly thirty percent of benzyl bromide is formed at 25°. Since sunlight increases the rate of the chain substitution it is probable that even more benzyl bromide would have been formed if the tubes had been exposed to direct sunlight. This conclusion is confirmed by some experiments that Bruner made on photobromination in a nitrobenzene solution. From Table III we see that only 1.3 percent benzyl bromide is formed at 25° and only 18.9 percent at 74°. When this same solution was exposed to direct sunlight, the yield of benzyl bromide jumped up to seventy percent.

While bromine and toluene react in the dark, it is stated by Schramm[2] that bromine does not react at an appreciable rate with *p*-bromtoluene or ethyl benzene in the dark. In sunlight there are formed *p*-brombenzyl bromide and phenyl ethyl bromide.

The results of the preceding pages are given in a condensed form in Table V.

TABLE V

Benzene and Chlorine

No reaction in dark.
Hexachloride in sunlight.
Hexachloride in the dark with H_2O or dil. NaOH.
Hexachloride with red phosphorus.
Some hexachloride with ICl in the dark.
Substitution with $FeCl_3$, $SnCl_4$, $SbCl_5$$MoCl_5$, Al_2Cl_6ICl, S, SO_2Cl_2, H_2SO_4, etc.
Substitution by electrolysis.
Some substitution in the dark with H_2 or dil. NaOH.

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[1] Ber. chem. Ges. Berlin, 18, 606 (1885).

[2] Ibid., 18, 350 (1885).

TABLE V—(*Continued*).

Benzene and Bromine

Up to 50% C_6H_5Br in the dark.
Hexabromide in sunlight.
Hexabromide in the dark with H_2O or dil. NaOH.
Substitution with $FeBr_3$, $FeCl_3$, IBr, etc.
Some substitution in the dark with H_2O or dil. NaOH.

Toluene and Chlorine

Ring and chain substitution in the dark, temperature effect.
Chain substitution in sunlight.
Chain substitution in the dark with H_2O or dil. NaOH.
Chain substitution with phosphorus pentachloride.
Chain substitution (nitrotoluene) with sulphur as carrier.
Some chain substitution in the dark with H_2O or dil. NaOH.
Ring substitution with $FeCl_3$, ICl, $SbCl_5$, etc.
Ring substitution by electrolysis.
Some ring substitution in the dark with H_2O or dil. NaOH.

Toluene and Bromine

Ring and chain substitution in the dark: concentration and temperature effect.
Ring and chain substitution with bromine and water.
Chain substitution in sunlight.
Chiefly chain substitution in sunlight in presence of nitrobenzene.
Chiefly ring substitution in the dark, in presence of nitrobenzene: temperature effect.
Ring substitution with $FeBr_3$, $FeCl_3$, etc.: concentration effect.
Ring (and chain) substitution with IBr: concentration and temperature effect.

Various explanations of the action of halogen carriers have been given. The following one is that of Page.[1]

"No satisfactory explanation of the action of chlorine carriers seems yet to have been given. There are two hypotheses which are worthy of special consideration.

"According to the first the chlorine carrier first combines with chlorine and then gives up that chlorine to the substance which is to be chlorinated. This process of com-

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[1] Liebig's Ann., 225, 203 (1884).

bining with chlorine and giving it up is then repeated. The following equations represent these reactions:

1. $MoCl_3 + Cl_2 = MoCl_5$.
2. $C_6H_6 + MoCl_5 = C_6H_5Cl + HCl + MoCl_3$.
3. $MoCl_3 + Cl_2 = MoCl_5$

and so on.

"In order to explain the process of chlorination by means of this hypothesis, one must assume that less energy is required to overcome the attraction by which the active chlorine is held to the molecule of the halogen carrier than is required to break the bond which holds the two atoms in the molecule of chlorine gas. The halogen carrier therefore converts the chlorine into a state similar to that of atomic chlorine, in which the reacting power of the halogen seems to be increased considerably. The following facts appear to be against this view:

"(a) *The difference in the action of chlorine on toluene, according to whether a halogen carrier is or is not present.*—If chlorine is led into boiling toluene, substitution takes place in the methyl group. This proves, what is also confirmed by other reactions, that substitution takes place more readily in the methyl group than in the benzene radical. We should therefore expect that, when either atomic or molecular chlorine acts on toluene, the hydrogen of the methyl group would first be replaced and that the hydrogen of the phenyl group, since it reacts less readily, would either not be replaced at all or only after the substitution in the methyl group was completed. Instead of this, the presence of a chlorine carrier causes a reversal of the behavior of toluene towards chlorine, substitution beginning in the phenyl group and ending in the methyl group. Such a reversal cannot be explained by any assumption in regard to a halogen carrier producing atomic chlorine.

"(b) Further, if the action of the halogen carrier consists in a simple giving off of chlorine, the halogen carrier must be reduced if it reacts in absence of chlorine with the substance to be chlorinated. To test this experimentally, 10 cc of benzene with 1.82 g of Fe_2Cl_6 were heated to 100° in a sealed tube. On opening the tube no pressure was noticeable and very little hydrochloric acid was evolved. Part of the benzene was charred and formed a black tarry mass with the ferric chloride. Neither in the liquid nor in the black residue could ferrous salt be detected. Therefore, the action of ferric chloride as a halogen carrier cannot consist in an alternate reduction to ferrous chloride and conversion back to ferric chloride. It still remained to determine whether dissolved ferric chloride might not take up chlorine as does lead chloride. When 60 g Fe_2Cl_6 were dissolved in 50 cc H_2O and the solution saturated with chlorine, no considerable increase in weight could be detected either at ordinary temperature or at higher temperatures.

"A second assumption seems to me to be more plausible, namely that *the halogen carrier and the substance to be chlorinated form a molecular compound* and that this compound is then decomposed by chlorine with formation of HCl and a chlorine substitution product. This reaction can be represented by the equations:

(1) $C_6H_5CH_3 + Fe_2Cl_6 = C_6H_5(Fe_2Cl_6)CH_3$.

(2) $C_6H_5(Fe_2Cl_6)CH_3 + Cl_2 = C_6H_4ClCH_3 + HCl + Fe_2Cl_6$.

"This offers an explanation of the facts that the substitution occurs first in the phenyl group when a benzene derivative is chlorinated in presence of a halogen carrier and that the chlorination of a benzene compound is easier than that of a fatty compound because the ferric chloride adds on more readily to the benzene radical.

"This process of chlorination is perhaps analogous to the behavior of ferric chloride and water. Ferric chloride crystallizes with water. When this compound is heated in the air, a rearrangement takes place inside the molecule, in consequence of which hydrochloric acid passes off and not water, ferric oxide remaining behind. If, however, this compound, which contains water, is heated with hydrochloric acid gas, the $Fe_2(OH)_6$, which one may assume to be first formed, takes up Cl again. First, water distils over and then anhydrous ferric chloride.[1] Ferric chloride behaves in the same way towards alcohol as towards water.

"Perhaps a more appropriate example is the reaction between aluminum chloride and benzene, studied by Gustavson.[2] This forms a compound, $Al_2Cl_6.6C_6H_6$ with benzene; aluminum bromide forms a corresponding compound. Bromine reacts violently with both compounds, forming C_6Br_6. Aluminum chloride behaves similarly with toluene and other aromatic hydrocarbons. It may therefore be assumed that ferric chloride forms corresponding compounds."

Scheufelen[3] has the following to say on the same subject.

"No thoroughly satisfactory explanation has yet been offered to account for the action of these bromine and chlorine carriers.

"Page[4] believes that a molecular compound is formed from the halogen carrier and the substance to be chlorinated, and that this compound is then decomposed by chlorine with formation of hydrochloric acid and a chlorine substitution product. In agreement with this are also the observations of Gustavson,[5] who has shown the existence of a compound of benzene and aluminum chloride or aluminum bromide, with both of which compounds bromine reacts violently, forming hexabrombenzene.

"I shall now show that my experiments furnish, as I hope, an important contribution to the better understanding of these processes.

"If one lets bromine act on nitrobenzene and ferric chloride, there is formed bromnitrobenzene, ferric bromide, and hydrochloric acid. The reaction with benzene runs in the same way. Since the ferric chloride is converted almost completely into ferric bromide, it is not probable that hydro-

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[1] Deville and Troost: Comptes rendus, 52, 920.

[2] Ber. chem. Ges. Berlin, 11, 2151 (1878).

[3] Liebig's Ann., 231, 191 (1885).

[4] Ibid., 225, 203 (1884).

[5] Ber. chem. Ges. Berlin, 11, 2151 (1878).

chloric acid is a secondary product resulting from the action of hydrobromic acid on ferric chloride, although I assured myself by a special experiment that hydrobromic acid gas dried with phosphorus pentoxide, is able to set free hydrochloric acid in no inconsiderable amounts from ferric chloride which is partly dissolved in benzene and partly suspended in it.

"Page[1] made one experiment in which 10 cc of benzene and 1.82 g of ferric chloride were heated in a sealed tube to 100°; no ferrous salt could be detected among the reaction products. From this experiment it follows that ferric chloride alone cannot chlorinate benzene by giving off chlorine. If, now, bromine is also present, one atom of chlorine can tear itself loose from the iron and can combine with one atom of hydrogen from the benzene to form hydrochloric acid because at the same time the bromine molecule is split up and its atoms can saturate the free affinities of the iron and the benzene. If one looks upon the reaction as taking place in this way, it is easy to see that all the ferric chloride may be converted into ferric bromide.

"Chlorination in presence of ferric chloride probably takes place in the following way. The chlorine of the ferric chloride combines with the hydrogen of the benzene and at the same time the free chlorine molecules split into atoms, some of which combine with the benzene radical and the rest with the iron. The atoms of chlorine which have combined with the iron are now able to form hydrochloric acid again and to cause the same round. The chlorination can therefore be brought about by a much smaller amount of ferric chloride than corresponds to the hydrochloric acid formed.[2] The experimental results confirm this conclusion."

Willgerodt[3] quotes the preceding paragraph from Scheu-

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[1] Liebig's Ann., 225, 205 (1884).

[2] The whole process, being a reaction between *three* substances, is obviously analogous to the remarkable oxidations which have recently been studied thoroughly by Mr. Traube. Ber. chem. Ges. Berlin, 18, 1877 (1885). *Lothar Meyer.*

[3] Jour. prakt. Chem. [2], 34, 290 (1886).

felen's paper, and then goes on: "Since benzene and the hydrocarbons derived from it cannot be chlorinated direct with ferric chloride at room temperatures, while chlorine and bromine even without a carrier form substitution products, I cannot adopt this view. For a long time I have held the view, expressed by Page, that the effectiveness of the halogen carriers is due to their forming molecular addition compounds with the aromatic substances, and to these molecular compounds being more easily attacked by the halogens than are the free organic substances themselves. This view of ours is supported by the fact that the halogen always substitutes in the aromatic ring when a halogen reacts in presence of a halogen carrier with an aromatic compound having aliphatic side chains. This view is also supported by the work of Gustavson[1] during which he succeeded in preparing the compounds $Al_2Cl_6.6C_6H_6$ and $Al_2Cl_6.6C_7H_8$. I suspect that the hydrocarbon molecules in these compounds do not all act exactly alike, which is quite conceivable. It is always quite probable that only one of them is united chemically with the aluminum chloride while the remaining five act as hydrocarbons of crystallization. The molecular compounds of benzene with Al_2Cl_6 or Fe_2Cl_6 (perhaps such oxychlorides as BiOCl may act similarly) must then be represented somewhat differently, depending on whether one starts with the benzene formulas of Kekulé, Claus, or Ladenburg. This is only conceivable, however, in case one assumes that one of the double or diagonal bonds of the benzene ring is broken and that the two valences set free thereby are neutralized by the inorganic halide, which can happen if the latter splits into a halogen atom and a univalent compound radical. If such an addition compound is brought in contact with the halogens, chlorine or bromine, a reaction takes place in such a way that a halide acid and an organic substitution product are formed while the inorganic halide is either regenerated or converted into another equivalent with respect to halogen. The halide acid is probably split

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[1] Ber. chem. Ges. Berlin, 11, 2151 (1878).

off from just one carbon atom, the organic and the inorganic halogen compounds by one halogen atom of the reacting molecule combining with this C atom while the other adds on to the compound inorganic radical. In this way it is possible to explain the forming again of the bond broken by the addition in the aromatic substance, and the substitution of hydrogen by the halogens. In violent reactions, it is conceivable that two halogen atoms might react simultaneously with the addition compound. In such cases the second molecule would substitute at the point to which the inorganic radical is attacked, and a di-substitution product would then be formed."

Since both Page and Scheufelen were pupils of Lothar Meyer, this expression of Willgerodt's views called forth an answer from Lothar Meyer. After commenting on Willgerodt's hypothesis that the ability of the elements to act as halogen carriers is a function of their atomic weights, Meyer[1] proceeds as follows:

"More important than these speculations according to my judgment is the question as to the real way in which halogen carriers act. At the end of the paper in question, Mr. Willgerodt says that he cannot agree with the view expressed by Scheufelen and that he is more in sympathy with the explanation offered by Page. There is, however, no conflict between these two views. Page considers it probable that the halogen carrier first forms a molecular compound with the hydrocarbon and that the free halogen decomposes this. Scheufelen showed that the reaction took place in such a way that the chlorine of the carrier combines with the hydrogen of the hydrocarbon, and the two are replaced each by one atom from the free halogen. This is no hypothetical opinion but an experimentally proved fact, for ferric chloride, bromine, and benzene form hydrochloric acid, ferric bromide, and brombenzene. Iodine acts similarly, though here, as one of my students, Mr. Schmidt, has recently

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[1] Jour. prakt. Chem. [2], 34, 503 (1886).

noticed, the reaction soon ceases owing to a change having taken place represented by the equation:

$$Fe_2Cl_6 + I_2 + C_6H_6 = FeCl_5I + HCl + C_6H_5I.$$

In my opinion, these are very remarkable facts and I do not wish to see them ignored. For this reason I consider it advisable to emphasize them again here. Mr. Willgerodt remarks very truly that our knowledge in regard to halogen carriers cannot be considered as forming a closed chapter. The less this is the case, however, the more careful we must be to make certain of each step gained in our knowledge so as to be able to mount again from it."

The arguments in favor of the assumption of an intermediate compound and against any other explanation are apparently three:

(1) No hypothesis in regard to active chlorine can account for the reactions between chlorine and toluene.

(2) Ferric chloride alone does not react with benzene and ferric chloride does not take up chlorine.

(3) Aluminum chloride can form a crystalline compound with benzene or toluene.

The first argument falls to the ground if we succeed in framing a hypothesis which will account for the formation of chlortoluene in presence of a carrier and of benzyl chloride when no carrier is present. Since one object of this paper is to present such a hypothesis, it will be better to discuss the other two arguments first.

The second argument is that any explanation except that of the intermediate compound is impossible because ferric chloride alone does not react with benzene and because ferric chloride does not take up chlorine. The orthodox way of meeting a difficulty like this, is first to dispute the accuracy of the facts and then to point out that the facts do not prove anything even if they are as stated. I intend to avail myself of both of these methods of defense.

As regards the accuracy of the facts we have Seelig's statement[1] that ferric chloride and toluene begin to react at about 60° and that ferrous chloride is formed. This evidence is not as satisfactory as I could wish it to be. Seelig apparently let the temperature run up so that some of the toluene charred and he does not state definitely that chlortoluene was formed though he implies it. Slator[2] found that benzene and iodine monochloride react in the sunlight forming monochlorbenzene, hydrochloric acid and iodine. Müller[3] states that benzene and antimony pentachloride react. We thus have two cases in which the halogen carrier is reduced by the aromatic compond. It seems to me more than probable that this could be duplicated with molybdenum pentachloride, with antimony pentachloride and with phosphorus pentachloride. In fact, Page's own experiments are not conclusive. Some reaction took place because the benzene was charred, which certainly would not have happened at 100° if no ferric chloride had been present. It is quite possible that the reaction might have taken place smoothly at a somewhat lower temperature if the tubes had been exposed to bright sunlight.[4] Slator found that the rate of reaction between benzene and iodine monochloride was practically negligible in the dark but that there was no difficulty about the reaction in bright sunlight. Considering the matter from the view-point of twenty-four years later, it is easy to see that the conditions of the experiment, which seemed best to Page (really to Lothar Meyer) in 1884, were admirably contrived so as not to throw any light on the subject at all. The most that anybody can claim for Page's conclusion is that it is not proved.

No valid conclusion can be drawn from Page's experiment in which he passed chlorine into a concentrated ferric chloride solution and found that no important increase of

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[1] Seelig: Liebig's Ann., 237, 169 (1887).

[2] Zeit. phys. Chem., 45, 532 (1903).

[3] Jour. Chem. Soc., 15, 43 (1862).

[4] This prediction has since been realized experimentally by Mr. Schluederberg in my laboratory.

weight took place. If one is going to assume the existence of $FeCl_5$, one is not obliged to assume the existence of a large amount of it. We may have a reversible equilibrium between $FeCl_5$, $FeCl_3$ and Cl_2 without having anything more than the merest trace of $FeCl_5$ in the solution. This argument of Page's is, therefore, not sound. I do not care to lay very much stress on this point because I have no desire, myself, to assume the existence of $FeCl_5$; but it is only fair to point out that there is nothing in Page's work which prevents one from assuming the existence of such a compound if he so wishes.

Having thus shown that the facts are not necessarily as Page thought they were, we can now show that Page's argument does not hold even on his own statement of facts. For the sake of argument, we will grant that neither ferric chloride nor iodine monochloride will react either with benzene or toluene when there is no excess of chlorine. That does not prove in any way that ferric chloride will not react with benzene when an excess of chlorine is present. An illustration will make this clearer. Sunlight will not reduce ferric chloride in aqueous solution, because the reaction products would be ferrous chloride and chlorine (possibly some hypochlorous acid) which would give an electromotive force greater than that of light. In presence of alcohol, light can reduce ferric chloride, because the alcohol acts as a depolarizer for chlorine. Now, it might easily be that ferric chloride does not react with benzene because of the ferrous chloride that would then be formed. The reaction might, however, take place if we removed the ferrous chloride by means of a suitable depolarizer such as free chlorine. This suggests the possibility of making ferric chloride react with benzene by means of an oxidizing agent less powerful than chlorine. I have not been able to find any record of anybody having tried this experiment but I hope to have it tried before long. The important thing for the moment is to show that ferric chloride might conceivably react with benzene in presence of chlorine even though it did not in the absence of chlorine.

We can now consider Page's argument in favor of the reaction being due to the intermediate formation of an addition compound or molecular compound, so-called. At the time that Page put forward this hypothesis, it was unquestionably the one having the most evidence in its favor. In the last twenty years, however, there has been a good deal of new evidence, all of which tends against this explanation. Cohen[1] has shown that chlortoluene is formed when toluene and concentrated hydrochloric acid are electrolyzed between carbon electrodes. It is difficult to see what intermediate addition can be assumed here, and yet, if we can get substitution in the ring in some cases without assuming the existence of an intermediate compound, the burden of proof is on the man who tries to show that there are two fundamentally different ways of accomplishing ring substitution. Schramm's work with bromine and toluene is also disconcerting because bromtoluene is practically the only product when the solution is kept cold and out of the light. Under certain conditions of temperature and concentration, free halogen does substitute practically exclusively in the ring. With bromine and toluene we get ring substitution in three sets of cases:

(1) With halogen alone, solution cold and dark.

(2) With halogen and halogen carrier.

(3) With electrolytically produced halogen.

Page said that the first case could not occur; he accounted for the second by the assumption of an intermediate compound; and the third case he did not know anything about. This in itself would be sufficient to show the inadequacy of Page's hypothesis, but this is not all. Within the last ten years, reaction velocity measurements have been made and these measurements do not confirm the hypothesis of Page. Bruner[2] finds that the rate of bromination of benzene and of toluene is proportional to the concentration of the hydro-

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[1] Jour. Chem. Soc., 87, 1034 (1905).

[2] Zeit. phys. Chem., 41, 513 (1902). Bull. Acad. Sci. Cracovie, 1907, 691.

carbon, to the concentration of the bromine and to the square of the concentration of the iodine monobromide. Slator[1] studied the rate of chlorination of benzene in presence of different catalytic agents and found that the rate was proportional to the concentration of the benzene, to the concentration of the chlorine, and to the concentration of the ferric chloride or stannic chloride when these were used as catalytic agents. When iodine monochloride was used as a catalytic agent, the rate was proportional to the square of its concentration and not to the first power of it. Now, of course, an experiment in reaction velocity is not an absolutely safe guide because there may easily be several ways of accounting for a given result, as indeed Slator[2] points out in this very case. On the other hand, a hypothesis which is not compatible with the kinetic measurements cannot be right. It is difficult to see how the rate can be proportional to the first power of the benzene concentration and the first power of the ferric chloride concentration if we postulate the intermediate formation of a compound of the type $Fe_2Cl_6.6C_6H_6$. Even if this difficulty were surmounted, we should still have to account for the rate being proportional to the square of the concentration in the case of the iodine monochloride and monobromide. I do not mean to say that both these difficulties might not be overcome by some ingenious man; but he would still be confronted by the three facts that bromine substitutes in the ring without a carrier, that electrolytic chlorine substitutes in the ring, and that phosphorus pentachloride is a carrier substituting in the chain. For the present, at any rate, we are justified in concluding that the arguments in favor of an intermediate compound and against any other explanation are not valid and that we are ready for an entirely fresh start.

Bruner[3] has offered an explanation of some of the reaction velocity relations when bromine reacts with toluene forming

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[1] Zeit. phys. Chem., 45, 513 (1903).

[2] Ibid., 45, 553 (1903).

[3] Bull. Acad. Sci. Cracovie, 1907, 718.

bromtoluene under one set of conditions and benzyl bromide under other conditions.

"The chief difference between the two reactions is, after all, the difference in the temperature coefficient, which determines the distribution at different temperatures. If we examine, for instance, the list given by van't Hoff of the temperature coefficients of different reactions so far as determined, it is distinctly noticeable that these are in general higher, the more complicated the substances that enter into the reaction, the highest values, 6–7, being observed with enzymes. The smallest on the other hand (1.2–1.3) are for the dissociation of arsine and phosphine (determined at higher temperatures, it is true) where we are compelled by the reaction being monomolecular, to assume that the first decomposition is into free atoms.[1]

"If one takes this into account, together with the fact that electrolytic halogen, which we usually consider as *in statu nascendi*, forms only substitutions in the ring even with boiling toluene, it seems very probable that the ring substitution is effected by other chemical individuals than those concerned in the chain substitution. The extraordinary photochemical sensitiveness of the chain substitution and the lack of sensitiveness to light of the ring substitution are to be cited as evidence in favor of the hypothesis. The simplest explanation would be to assume that the chain substitution was due to the bromine molecule, present in relatively large amounts, and the ring substitution to the free Br atoms[2] which, though present in relatively very small amounts, are much more ready to react. The formulation of the two reactions would then be as follows:

(1) $C_6H_5CH_3 + Br_2 = C_6H_5CH_2Br + HBr.$

(2) $C_6H_5CH_3 + 2Br = C_6H_4BrCH_3 + HBr.$

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[1] It may be mentioned here that subatomic (radio-active) changes are entirely unaffected by temperature changes.

[2] Cf. Bruner: Bull. Acad. Sci. Cracovie, 1902, 181; Zeit. phys. Chem., 41, 524 (1902).

"The two equations give the same monomolecular reaction with respect to the change of the bromine concentration with the time, provided one assumes, what has often been proved by molecular weight determinations, that most of the bromine is present as Br_2 and that the bromine is only very slightly dissociated into atoms.[1]

"Then according to the relation

(3) $$Br + Br \rightleftarrows Br_2$$

we have $(Br)_2$ proportional to (Br_2) which is the concentration of the bromine as determined by titration or by weighing.

"This formulation is in harmony with the recognized fact that the reaction is monomolecular in the absence of a catalytic agent. If iodine (iodine bromide) is added, the concentration of the Br atoms is determined both by the equilibrium

$$Br + Br \rightleftarrows Br_2$$

and also by the dissociation of the iodine bromide

(4) $$IBr \rightleftarrows I + Br$$

and the (Br) concentration is therefore proportional to the concentration of the (IBr). The equilibrium of the bromine atoms must be satisfied both with reference to equation 3 and equation 4; consequently the rate of consumption of the bromine atoms will be, according to equation 2 and in agreement with the experimental data previously given:[2]

$$-\frac{d\,[\text{Bromine}]}{dt} = k_1\,[Br]^2 = k_1\,[Br_2]$$

and on addition of iodine

$$-\frac{d\,[\text{Bromine}]}{dt} = k_1\,[Br_2] + k'_1\,[Br_2][IBr]^2.$$

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[1] Cf. Bruner: Zeit. phys. Chem., 41, 524 (1902). Slator: Ibid., 45, 553 (1903).

[2] In the paper so often referred to, Slator remarks quite truly, in connection with Prof. R. Luther's exposition, that different formulations of a reaction may be compatible with the kinetic equations. It would however be unwise not to make some attempt at an explanation and formulation of the reactions, especially if there are also other reasons which may serve to support a given formulation.

"From this point of view, the variation from the quadratic law at higher temperatures must be only a superficial one caused by the unknown and therefore unheeded dissociation relations of the iodine bromide.

"The experiments to be described give some information as to the nature of the bromine atoms, which we assume to be formed by the dissociation of the bromine and the iodine bromide. It seems probable that we must consider them as ions."[1]

In some experiments with bromine, toluene and nitrobenzene, the reaction velocity constant was not satisfactory. Bruner attributes this disturbance to the action of hydrobromic acid, which is somewhat soluble in nitrobenzene. He then proceeds.[2]

"Next to the disturbed course of the reaction we have *the strongly marked preponderance of the ring substitution products* as a peculiarity of the reaction in nitrobenzene. This phenomenon is certainly connected with the fact that bromine and a *portion* of the acid of the polybromides is dissociated into ions in nitrobenzene as solvent.[3] Even though the strong, mutually influenced ions, such as the chlorine or bromine anions of hydrochloric or hydrobromic acid, have no direct chlorinating action, it is however very plausible that the free halogen atoms, resulting from the neutralization of the electrical charges, might cause ring substitution by preference. Attention may also be called to the important fact noticed by J. B. Cohen[4] and his co-workers, that chlorine set free electrolytically at a carbon anode causes ring substitution exclusively, even in boiling toluene. The halogen atoms, thus formed, are incapable of substituting in the chain."

In the main I agree with this explanation of Bruner's.

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[1] L. Bruner: "On the Electrolytic Conductivity of Bromine and Iodine." Bull. Acad. Sci. Cracovie, 1907, 731.

[2] Bruner: Bull. Acad. Sci. Cracovie, 1907, 726.

[3] Ibid., p. 731.

[4] Jour. Chem. Soc., 87, 1034 (1905).

It is good as far as it goes; but it seems to me that the theory does not take cognizance of the following three items:

(1) The electrochemical action of light.

(2) The formation of benzyl chloride with water as a carrier.

(3) The formation of benzyl chloride with phosphorus pentachloride as a carrier.

We know that light of a proper wave-length increases the conductivity of most gases, apparently by forming ions. We must therefore find some difference other than that between the bromine molecule and the bromine atom so-called if we are going to account for the two different ways in which bromine and toluene react. If sunlight forms atoms or ions or anything else out of bromine or chlorine, we shall probably get products, one-half of which may be called positive and the other half negative. No assumption is made as to what we mean by positive and negative. If the dissociation products are ions, the words have their usual meaning. If the dissociation products are not ions, the words have another meaning. It will simplify matters, perhaps, if we speak of the hypothetical dissociation products as gaseous ions though this is not an essential part of the explanation. In an aqueous solution of chlorides or bromides we have negative chlorine anions or bromine anions but no chlorine cations or bromine cations. When these ions are discharged electrolytically, we have at first solely negative hypothetical chlorine or bromine gaseous ions. If there is nothing with which these hypothetical substances can react, there will necessarily be a re-arrangement of some sort and the formation of chlorine or bromine gas. If there is some substance present with which they can react, they will react so far as possible, as negative ions. With this as a starting point, I make the following assumptions in order to account for the reactions between bromine and toluene for instance.

(1) There is a slight reversible dissociation of bromine into positive and negative particles or gaseous ions.

$$Br_2 \rightleftarrows Br^+ + Br^-$$

(2) There is a slight reversible reaction between bromine and the positive gaseous ion.

$$Br_2.Br^+ \rightleftarrows Br_2 + Br^+$$

(3) Substitution takes place in the ring when the negative gaseous ions are present in excess; otherwise it takes place in the side chain.

(4) The addition products of benzene are to be considered as analogous to the chain substitution products of toluene.

(5) There is a reversible dissociation of the halogen carriers with formation of so-called gaseous halogen ions. Whether these ions are positive or negative depends on the nature of the carrier.

Of these assumptions the first and fourth are not new; the first half of the fifth has been made implicitly by everybody who has tried to account for halogen carriers without postulating the formation of an intermediate compound. It was made explicitly by Bruner. The second half of the fifth assumption is new but is a necessary consequence of the first part of the assumption.

The second assumption is new, so far as I know, and is made because I cannot get along without it. The third assumption is also new but is a necessary consequence of the first two assumptions.

I will now show how these assumptions apply to the cases which we have to account for. At low temperatures and in the dark, there will be a formation of $Br_2.Br^+$ and consequently an excess of Br^-. The relative excess will be greater, the greater the concentration of the bromine. We should therefore expect ring substitution in concentrated solutions with an increasing percentage of substitution in the side chain as we start with a more and more dilute bromine solution. This is exactly what was found by Bruner and some data illustrating the point were given in Table I. With rising temperature we get increasing dissociation of $Br_2.Br^+$, the ratio of Br^+ to Br^- increases, and consequently we should get an increasing percentage of benzyl bromide among the reaction products. This was also found experimentally by Bruner and some data were given in Table II. Sunlight will increase the dissociation of Br_2 and $Br_2.Br^+$ and will therefore bring the ratio of Br^+ to Br^- up very close to unity and consequently under the third assumption we shall get side chain substitution only, provided the intensity of the light is sufficient. In diffused light we shall of course get a state of things intermediate between the results for darkness and for bright light. Both of these predictions have been confirmed experimentally.

With a carrier such as ferric chloride our fifth assumption calls for a reversible dissociation into gaseous halogen ions and ferrous chloride. With iron we can, of course, only have negative gaseous halogen ions and the equilibrium will be represented by the equation

$$Fe_2Cl_6 \rightleftarrows 2FeCl_2 + 2Cl^-.$$

Under these conditions there will be enough negative gaseous ions from the ferric chloride to overbalance any positive ions which might come from the chlorine gas and we should expect to get ring substitution even in boiling toluene and even when the system is exposed to bright sunlight. This is exactly what happens.

With the chlorides of iron, antimony, molybdenum and aluminum, there can be no question but that chlorine is the negative radical. With iodine monochloride, however, the matter is more open to doubt. Since chlorine is a more powerful oxidizing agent than iodine, we might reasonably expect that iodine would be the positive radical and chlorine the negative radical. The margin of safety is not large however and the experimental results are just what we should expect under these circumstances. Iodine monochloride as carrier does substitute in the ring; but the dissociation is not sufficient to prevent substitution in the side chain in boiling toluene, especially if the concentration of iodine monochloride or monobromide be low. Of course, if one were to decrease sufficiently the concentration of ferric chloride as carrier there would come a point at which chain substitution would also occur in boiling toluene in spite of the iron; but no such point has been determined experimentally.

According to Slator's[1] experiments iodine monochloride is so near on the line that both addition and substitution products are formed when chlorine, iodine monochloride and benzene are brought together in the dark. With benzene and iodine monochloride alone practically no reaction takes place in the dark, presumably because the chemical potential is not sufficiently high to set free iodine. The action of sunlight so increases the dissociation of the iodine monochloride that the reaction can now take place. As was to be expected only negative gaseous chlorine ions are set free and chlorbenzene is the sole product. This is an especially interesting case because we have here a photochemical ring substitution, the existence of which is denied by Bruner. Corresponding experiments with toluene and iodine monochloride or monobromide in sunlight have not been made; but such experiments, when made, will undoubtedly confirm the theory. In some cases iodine monochloride can be used to prepare iodine substitution products.[2]

While iodine monochloride is on the line, phosphorus pentachloride is apparently over it and either forms positive gaseous chlorine ions only or an equal quantity of positive and negative gaseous chlorine ions. It makes no difference which reaction we postulate,

$$PCl_5 = PCl_3 + 2Cl^+$$

or

$$PCl_5 = PCl_3 + Cl^+ + Cl^-.$$

Either one will account for the formation of benzyl chloride by the action of chlorine and phosphorus pentachloride on toluene.[3] Since the phosphorus pentachloride accelerates

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[1] Zeit. phys. Chem., 45, 521 (1903).

[2] Lassar-Cohn: Arbeitsmethoden, 3rd Ed., 409.

[3] Colson and Gautier: Ann. chim. Phys. [6], 11, 19 (1887); Erdmann: Liebig's Ann., 272, 150 (1893).

the rate, we must look upon it as a halogen carrier. This differs from the case of the iodine monochloride because chain substitution takes place with phosphorus pentachloride and chlorine in sunshine. Willgerodt has shown that phosphorus pentachloride, chlorine and benzene form benzene hexachloride, so that its behavior with benzene corresponds to the behavior with toluene.

With the two non-metallic halides, iodine monochloride and phosphorus pentachloride, we have evidence of more or less well-marked tendency to form positive gaseous chlorine ions. This same tendency is also shown by sulphur chloride. Willgerodt[1] states that sulphur acts as a halogen carrier with benzene, forming chlorine substitution products. On the other hand Häussermann and Beck[2] have prepared *o*-nitrobenzyl chloride by letting chlorine act on *o*-nitrotoluene in presence of sulphur as a carrier. In this case it looks as though we had the formation of positive gaseous chlorine ions.[3]

A still more interesting case from the theoretical point of view is Matthews' synthesis of benzene hexachloride by passing chlorine through a mixture of benzene and water or dilute caustic soda. Goldberg[4] says that at present we can only make guesses at the mechanism of this reaction. It does not seem to me that matters are quite so bad as that. If we pass chlorine into water we get a reversible equilibrium represented by the equation

$$Cl_2 + H_2O \rightleftarrows HCl + HClO.$$

Since this is a reversible reaction, there is a continuous formation and consumption of chlorine. As a preliminary step to the formation of Cl_2 we have the setting free of Cl^- from the hydrochloric acid and of Cl^+ from the hypochlorous

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[1] Willgerodt: Jour. prakt. Chem. [2], 34, 264 (1886).

[2] Ber. chem. Ges. Berlin, 25, 2445 (1892).

[3] Chlorination by means of sulphuric acid appears to depend on the formation and decomposition of a sulphuric acid compound, and sulphuric acid is therefore not a halogen carrier of the same type as the others.

[4] Zeit. wiss. Photochemie, 4, 63 (1906).

acid. If benzene is present, these intermediate products of course react with it forming benzene hexachloride. This synthesis is therefore a necessary consequence of our third assumption and is an additional justification of it. If the chlorine gas combines to a certain extent with the positive gaseous ion, we shall get ring substitution to a greater or lesser extent.

The explanation of the action of halogen carriers is in accord with the reaction velocity measurements. It has already been pointed out that the rate is proportional to the first power of the concentration of the ferric chloride or the stannic chloride; but to the second power of the concentration of the iodine monochloride. This is a necessary consequence of the following equations:

$$C_6H_5CH_3 + 2Cl^- = C_6H_4ClCH_3 + HCl$$

$$Fe_2Cl_6 \rightleftarrows 2FeCl_2 + 2Cl^-$$

$$SnCl_4 \rightleftarrows SnCl_2 + 2Cl^-$$

$$2ICl \rightleftarrows 2I^+ + 2Cl^-.$$

Bruner's reasoning in regard to iodine monochloride is applicable without change to ferric chloride and stannic chloride. Since we have the relation

$$Cl_2 \rightleftarrows Cl^+ + Cl^-$$

the rate of chain substitution with toluene will be proportional to the concentration of the chlorine. The rate of formation of benzene hexachloride will be of the first, second, or third order with respect to chlorine, depending on which of the following reactions is the one actually measured:

$$C_6H_6 + Cl^+ + Cl^- = C_6H_6Cl_2$$

$$C_6H_6 + 2Cl^+ + 2Cl^- = C_6H_6Cl_4$$

$$C_6H_6 + 3Cl^+ + 3Cl^- = C_6H_6Cl_6.$$

It would strengthen the argument if it were possible to show why negative chlorine substitutes in the ring and positive chlorine in the side chain; but I do not see any explanation which can be carried through. We might assume that the hydrogen of the chain was positive and was therefore replaced by the positive chlorine and combined with the negative chlorine to form hydrochloric acid. In that case we should call the ring hydrogen negative. This hydrogen would be displaced by the negative chlorine, would change to positive in some unknown way and would form hydrochloric acid with the negative chlorine. This is not an unreasonable way of looking at things; but it does not account for the fact that ferric chloride is a bromine carrier. Lothar Meyer's contention seems to be sound, that the first step in the reaction is the formation of hydrochloric acid. Until some way is found of getting round this difficulty, we cannot do anything more than say that the assumption in regard to ring substitution is an assumption *ad hoc*, and that we cannot deduce it from anything else.

To a certain extent the chlorination or bromination of the aliphatic compounds follows the same general rules that have been laid down for the aromatic compounds; but this is by no means always the case. Hell and Gantter[1] have brominated the fatty acids with red phosphorus as a carrier and Volhard[2] has used the same method. Béhal and Anger[3] have chlorinated acetic acid with S or S_2Cl_2 as carrier. Melsens[4] has found that chloracetic acid is formed when sulphur dioxide and chlorine are passed into glacial acetic acid; but there is some question whether this is anything more than a coupled reaction. These cases are all in keeping with the assumption that we have positive gaseous chlorine ions with these carriers. The fact that iodine monochloride in boiling acetic acid acts as a chlorine carrier[5] might possibly pass, though it is rather stretching a point. Page[6] found that molybdenum pentachloride was not a carrier for aliphatic compounds and that ferric chloride in acetic acid was not a

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[1] Ber. chem. Ges. Berlin, 14, 891 (1881).
[2] Liebig's Ann., 242, 141 (1887).
[3] Bull. Soc. chim. Paris [3], 3, 144 (189).
[4] Comptes rendus, 76, 92 (1873).
[5] Müller: Jour. Chem. Soc., 15, 41 (1862).
[6] Liebig's Ann., 225, 196 (1884).

chlorine carrier. This is all as it should be; but any premature rejoicing is checked by the fact that ferric chloride is a chlorine carrier in alcohol. It is not difficult to find other cases of the same sort.[1] All that can be said at present is that those substances which ought to be halogen carriers for aliphatic compounds are halogen carriers; but that the converse is only occasionally true.

It may be asked what substances are halogen carriers for aromatic compounds. According to the explanation given in this paper, the other element in a halogen carrier must lose chlorine under the conditions of the experiment. It must either have two effective valences in regard to the halogen or must reduce readily to the element as in the case of iodine monochloride. Of course, the converse is not necessarily true, that every substance forming two chlorine compounds is necessarily a chlorine carrier. An apparent weak point in the argument is the behavior of aluminum. From the experiments of Goldschmidt and Larsen[2] we know that aluminum chloride behaves exactly like tin tetrachloride as a carrier. We must therefore have the following reactions taking place:

$$SnCl_4 = SnCl_2 + 2Cl^-$$
$$Fe_2Cl_6 = 2FeCl_2 + 2Cl^-$$
$$Al_2Cl_6 = 2AlCl_2 + 2Cl^-$$

Unfortunately no such substance as aluminous chloride is known at present. It was therefore necessary to demonstrate the possibility of such a compound. This was done by making aluminum anode in a chloride solution. When a heavy current density is used, aluminum dissolves with a lower effective valence as is shown by the instable salt breaking down and evolving hydrogen at the anode.[3] Though the aluminous chloride has not yet been isolated, its existence as an instable salt has been demonstrated sufficiently to account for the behavior of aluminum chloride as a halogen carrier.

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[1] Lassar-Cohn: Arbeitsmethoden, 3rd Ed., 305.
[2] Zeit. phys. Chem., 48, 424 (1904).
[3] Turrentine: Jour. phys. Chem., 12, 455 (1908).

The general conclusions are as follows:

(1) The action of halogen carriers is not due to the intermediate formation of addition compounds.

(2) Under suitable experimental conditions the halogen carriers react with benzene or toluene even when no free halogen is present.

(3) A theory of halogen carriers has been developed on the assumption of positive and negative dissociation products of the halogens.

(4) This theory is a development or amplification of Bruner's theory.

(5) The theory accounts for the catalytic action of ferric chloride, aluminum chloride, stannic chloride, iodine monochloride, phosphorus pentachloride, water and sunlight.

(6) The theory accounts for the reaction velocity relations with ferric chloride, stannic chloride, aluminum chloride, iodine monochloride and water.

(7) There is strong experimental evidence of the existence of aluminous compounds.

(8) The theory of Grotthuss has proved serviceable in explaining the action of halogen carriers.

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REVERSED ELECTROLYSIS

BY J. W. TURRENTINE

"In the case of electrolysis the only specific action which we have to attribute to the current is that it tends to set free the anions at the anode and the cations at the cathode."[1] At the anode this action may result in the formation of new cations due to the corrosion of the anode by the liberated anions. Employing a different terminology, these facts may be expressed as the diminution of electric charges on the cations at the cathode and the increase of like charges at the anode. The electric charges of an ion may be looked upon as the manifestation of valence if we regard valence as potential combining capacity. If we define oxidation or reduction as a change in valence and keep in mind the theory of valence changes, from either view point it is seen that at the cathode we have a reduction and at the anode, an oxidation. So, we may adopt as a rule that electrolysis in aqueous solution invariably leads to oxidation at the anode and reduction at the cathode.

Oxidation at the anode may be fully explained by the simple chemical action of the discharged anion, and reduction at the cathode by the action, likewise, of the discharged cation. Anions being electronegative in character, on being discharged at the anode they appear as strong oxidizing substances and either escape as such or corrode the anode or react with some oxidizable substance in the electrolytic bath. In an analogous manner may be explained the corresponding reduction at the cathode.

In pure chemistry we understand oxidation as meaning the addition of electronegative substances, as oxygen, or the subtraction of electropositive substances, as hydrogen, and a reduction as the reverse. Since either process may manifest itself as a change in valence or the number of electric changes

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[1] Bancroft: Trans. Am. Electrochem. Soc., 8, 33 (1905).

of the ion acted upon, the chemical and electrochemical oxidation-reduction phenomena are practically identical.

The reduction of one substance results in the oxidation of the reducing agent—which fact is as well-known as the law of the conservation of energy. The products of a reduction, however, may appear to be more potent reducing agents than the agent which induced the reaction leading to their formation. A parallel statement may be made in regard to the products of the oxidation of hydrazine by numerous oxidizing agents[1] yet the ratio of hydrogen to nitrogen is higher in ammonia than that in hydrazine, but the former is a weaker reducing agent than the latter on account of its greater stability. Likewise, the oxidation of phosphine by oxygen,[2] when the two gases, highly diluted by some neutral gas, are allowed to mix slowly by diffusion, results in the production of free hydrogen, according to the equation:

$$2PH_3 + 2O_2 = 2HPO_2 + 2H_2$$

yielding a product more highly reduced than the reducing agent itself, though, as in the previous case, more stable than the reducing agent.

Potassium permanganate and hydrogen peroxide act towards each other in acid solution as mutual reducing agents, each giving up a part of its oxygen.[3]

Depending on conditions, hydrogen peroxide may act both as an oxidizing and as a reducing agent, in either case giving up one-half of its oxygen.

Such irregularities may be explained on the basis of an intermediate reaction, though the existence of such a reaction cannot always be demonstrated. Secondary reactions may take place which effectively conceal the primary reaction so that the ultimate result may appear as a reduction by an oxidizing agent or an oxidation by a reducing agent.

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[1] Browne and Shetterly: Jour. Am. Chem. Soc., 29, 1305 (1907); 30, 53 (1908).

[2] Van der Stadt: Zeit. phys. Chem., 12, 322 (1893).

[3] Brodie: Jour. Chem. Soc., 7, 304 (1855); Lunge: Zeit. angew. Chem., 1890, p. 6.

In the electrolysis of aqueous solutions a reversal of the usual order of things, to which we have given the designation of reversed electrolysis, must always be considered as the result of secondary reactions since, from definition, the primary reaction is always one of oxidation at the anode and of reduction at the cathode. Such cases are numerous. Luther[1] shows that when Fehling's solution is electrolyzed, cuprous oxide is deposited on the anode as well as metallic copper on the cathode, a reduction resulting at both poles. The direct and primary action of the current is the oxidation of the tartaric acid to formic acid, an oxidation product but a less stable substance which reduces the cupric salt and precipitates on the anode cuprous oxide. In the same way gold can also be reduced and deposited, as, also, in methyl alcohol solution, if alkaline, when aldehyde is produced at the anode.

In an ammoniacal solution of potassium bromide, potassium permanganate is reduced to the green manganate at the anode. This result is brought about through the oxidation of bromide at the anode to hypobromite; this oxidizes the ammonium hydroxide to hydroxylamine which in turn reduces the permanganate, purple, to the manganate, green. Also, when a gold salt, or a permanganate, is present in a saturated solution of an alkaline carbonate, upon electrolysis, reduction occurs at the anode due to the formation there of percarbonates which, breaking down in the aqueous solution, yield as a product hydrogen peroxide. This acts as the reducing agent towards the gold and the permanganate.

Yet more striking is the reversal obtained when a dilute solution of nitric acid containing potassium iodide is electrolyzed—iodine being liberated at the cathode as well as at the anode. Nitric acid on electrolysis is reduced to nitrous acid. The latter reacts at once with potassium iodide, oxidizing it and liberating iodine against the cathode.

Tommasi,[2] on electrolyzing a solution of chloral hydrate,

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[1] Zeit. Electrochem., 8, 645 (1902).

[2] Electrochimie, 741.

obtained chlorine at the cathode. Wood and Jones[1] obtained a deposit of metallic copper simultaneously at both poles from a solution of the double carbonate of copper and potassium. This we may explain as we did the deposition of gold from the carbonate solution as due to a reduction by hydrogen peroxide which had been produced by the decompositions of percarbonates.

Kraus,[2] in his interesting work on solutions of metals in liquid ammonia, furnishes us with the most perfect instance of reversed electrolysis, though hardly comparable to the other cases cited as it does not have to do with aqueous solutions. When a solution of sodium in liquid ammonia is electrolyzed between lead electrodes lead is dissolved from the *cathode* and appears in the solution as negatively charged ions of Pb_2. The observed loss in weight of the cathode agrees almost perfectly with the value calculated from the electrochemical equivalent of lead.

Hydrogen at the Anode

Beetz[3] has described experiments in which he obtained an evolution of hydrogen from the anode when he electrolyzed a solution of magnesium sulphate between magnesium electrodes. Thin magnesium wire electrodes of the size of knitting-needles were projected through the bottom of a glass vessel. The anode, he noted, became covered by a black substance, supposed by the author to be a suboxide of magnesium, which slowly dissolved with an evolution of hydrogen and which, also, filled the solutions in the anode region, causing turbidity. As these phenomena would indicate a disintegration of the anode with subsequent decomposition of water by the finely divided magnesium (as the author himself deemed possible), a similar experiment was performed in connection with this paper, as follows:

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[1] Proc. Cam. Phil. Soc., 14, 11, 171 (1907).

[2] Jour. Am. Chem. Soc., 29, 1556 (1907).

[3] Phil. Mag., 32, 269 (1866); Pogg: Ann., 127, 45. Cf. also Elsässer: Ber., 9, 1818 (1876); 11, 587 (1878).

A solution of sodium sulphate (5 grams to 250 cc H_2O) was electrolyzed between a platinum cathode and a magnesium anode. The anode consisted of a bunch of magnesium ribbon sealed in the end of a glass tube by means of cerusine. The tube was bent back upon itself so that the anode in its end could be thrust into an inverted burette which served as eudiometer. An oxy-hydrogen gas coulometer was joined in series. The accumulated gas was withdrawn and analyzed over alkaline pyrogallol in a Hempel pipette. The residue, after being subjected to qualitative tests, was taken as hydrogen. Under the conditions of the experiment the current density at the anode could not be estimated nor maintained constant, so the different measurements obtained can hardly be compared with each other. It is seen from Table I that the evolution of gas from the anode was vigorous and, from the analysis, was almost pure hydrogen.

TABLE I

Gases from Magnesium Anode				Gases from Coulometer		
No.	T. V.	O_2	H_2	T. V.	O_2	H_2
	cc	cc	cc	cc	cc	cc
1.	31.2	1.0	30.2			
2.	18.8	0.6	18.2	28.2	9.4	18.8
3.	13.8	0.6	13.2	26.3	8.7	17.6
4.	9.4	0.8	8.6	30.5	10.2	20.3
5.	12.7	0.6	12.1	40.0	13.3	26.7
6.	14.4	0.4	14.0	40.5	13.5	27.0
7.	4.8	0.2	4.6	15.0	5.0	10.0

While the results shown in this table verified Beetz's observations as to the evolution of hydrogen, no indication was obtained of the formation of a black compound or of the disintegration of the anode. The corrosion of the anode was in every case rapid and led to the appearance of a voluminous white precipitate of magnesium hydroxide in the anode region. Bubbles of gas occasionally came off from the precipitate, but seemed to be merely the escape of the entangled hydrogen. The magnesium anode remained white and became covered with scales of magnesium hydroxide, periodically dislodged by the vigorous evolution of gas. On breaking the current the cessation of the evolution was not sharp, which fact would indicate the formation of some compound which gradually decomposed water. Such a substance could only be metallic magnesium or a compound of magnesium in which the effective valence of the magnesium is less than two. If the latter, it would be acting analogously to cuprous sulphate which, in cold solutions, breaks down and deposits metallic copper, and to chromous salts which react with water and evolve hydrogen.[1]

The absence of a visible change in the surface of the anode and yet a free evolution of hydrogen, persisting for a short time after the current had been broken, would make it appear that this decomposition of water is quite analogous to that by chromous salts. Instead of the product of the electrolysis appearing as a solid, as noted by Beetz, these experiments would rather indicate the actual solution of the anode as *magnesious* sulphate which at once reacted with the water of the electrolytic bath and formed *magnesic* sulphate and hydroxide, according to the equation

$$Mg_2SO_4 + 2H_2O = MgSO_4 + Mg(OH)_2 + H_2.$$

This reaction would account for the evolution of hydrogen and for the voluminous precipitate of magnesium hydroxide in the immediate region of the anode. The scale of magnesium hydroxide surrounding the anode, by allowing slow diffusion outward of the unstable salt, would afford an explanation of the continuation of the evolution of hydrogen after the interruption of the electrolysis.

Beetz made a series of quantitative measurements of the hydrogen evolved from the two poles and of the magnesium dissolved from the positive pole. In every case he found that the combined volumes of the gas evolved from the two

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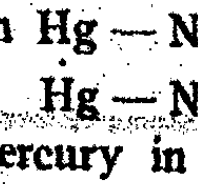
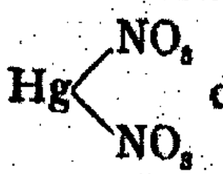
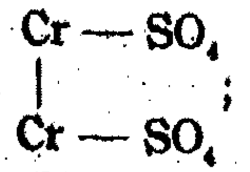
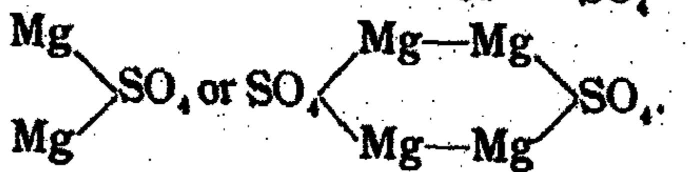
[1] Ufer: Liebig's Ann., 112, 302 (1859).

electrodes was approximately equivalent to the weight of the magnesium dissolved from the anode.

These measurements are not inconsistent with our assumption of the occurrence under these conditions of Mg with a lower valence, but they can not, from the nature of the case, prove the existence of such a form. Indeed, in the example mentioned above of the oxidation by water of an unstable compound, in which the metal is apparently oxidized from a lower to a higher valence, we may be dealing solely with a question of linkage of molecules and not with one of a change of valence. Mercurous nitrate, we know from the work of Ogg,[1] must be considered as $HgNO_3.HgNO_3$. If written  $\begin{array}{l}Hg-NO_3\\ \mid\\ Hg-NO_3\end{array}$, an actual difference in valence between the mercury in this molecule and that of the mercury in  $Hg\begin{array}{l}\diagup NO_3\\ \diagdown NO_3\end{array}$ does not exist.

To bring the structural formula for ferric chloride into agreement with certain of its reactions it must be considered as Fe_2Cl_6. Chromous sulphate may then be  $\begin{array}{l}Cr-SO_4\\ \mid\\ Cr-SO_4\end{array}$; magnesium sulphate may be .

But the matter of linkage is entirely aside from the question of valence as considered from the electrochemical standpoint. Linkage may exist. There may be no actual change in the valence of a metal. But there is an effective valence, based on Faraday's law and the electrochemical equivalents, which manifests itself in every electrolytic corrosion. It is with the effective valence that we have to do in this paper.

This belief in the lower valence of magnesium is substantiated by the work of others. Christomanos[2] obtained a

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[1] Zeit. phys. Chem., 27, 285 (1898).

[2] Ber. chem. Ges. Berlin, 36, 2076 (1903).

gray powder when he suddenly cooled a magnesium flame which, from its analysis, appears to have the formula Mg_8O_6, but which he regarded as a mixture of magnesium and magnesium oxide. Baborovsky[1] considers the suboxide obtained by Christomanos identical with that noted by Beetz. Considerable light could be thrown on this point if the compound prepared by Christomanos were placed in water; an evolution of hydrogen would strongly indicate the correctness of Baborovsky's contention.

White,[2] in his study of the action of solutions of bleaching powder on metals, observed that magnesium and aluminum are distinctive in that, while other metals studied, as iron, copper, nickel, etc., evolved oxygen, these two evolved hydrogen, the magnesium producing as much as 500 cc in twelve hours.

Luther and Schilow[3] employ the hypothetical magnesium of a valence of one to explain the reaction which takes place between iodine, methyl alcohol and magnesium,[4] in which hydrogen is evolved. Their supposition of an intermediate reaction in which is formed a *magnesious* iodide is represented by the equations:

$$Mg + 1/2\ I_2 = Mg\ I$$

$$Mg\ I + CH_3OH = Mg\ IOCH_3 + 1/2\ H_2.$$

In short, while the evidence adduced above does not establish the existence of monovalent magnesium, yet the chemistry and the electrochemistry of the metal demand the assumption of such a form.

Hydrogen at an Aluminum Anode

In the chlorination of organic compounds where the so-called "carriers" are employed, aluminum chloride, ferric chloride, and stannic chloride, all behave practically identi-

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[1] Ber. chem. Ges. Berlin, 36, 2719 (1903).

[2] Jour. Soc. Chem. Ind., 22, 132 (1903).

[3] Zeit. phys. Chem., 46, 803 (1903).

[4] "Data on the Chemical Rôle of Catalytic Agents," Jour. Russ. phys.-chem. Gesell., 35, 399; Chem. Centrlb., 711, 277 (1903).

cally. Ferric chloride and stannic chloride are both susceptible of a reduction to a lower chloride, thus furnishing an explanation of their rôle as catalytic agents in chlorination processes on the ground of intermediate reactions in which the ferric or stannic compound, in conveying chlorine into the molecule of the body to be chlorinated, is reduced to the ferrous or stannous compound, respectively, and is subsequently reoxidized, the oxidation taking place instantaneously. The close analogy between aluminum and iron and tin as carriers of chlorine made it seem probable that the analogy extended to the matter of valence, our lack of knowledge of aluminum compounds, in which the aluminum appears with a valence other than three, being absolute because of the great instability of such compounds. The position of aluminum in the periodic system, furthermore, being a close neighbor of both carbon and boron, makes it appear odd that this element does not exhibit the property of linkage as do both carbon and boron. The evidence obtained as to the dual nature of magnesium from the behavior of that metal when made anode led to the belief that a clue could also be gotten in the same way to the existence of aluminum with an effective valence lower than three. Accordingly, actuated by these considerations alone, we made aluminum anode in a solution of sodium chloride containing 10 grams of the salt to 200 cc distilled water. The same apparatus was employed here as that used in the like experiment with the magnesium anode.

A strip of aluminum foil was sealed, by means of cerusine, in a glass tube so bent that the exposed end of the foil, which was to serve as anode, could be projected into the mouth of an inverted burette to serve as eudiometer. Each face of the anode was about a square centimeter in dimensions. For cathode was employed a strip of platinum foil. A gas coulometer was joined in series with the electrolytic cell. The accumulated gases were withdrawn from the eudiometer into a Hempel gas burette, were measured and were then analyzed for oxygen by shaking with alkaline pyrogallol in a Hempel pipette. The residual volume, which gave affirmative qualitative tests, was taken as hydrogen. The results are given in Table II.

TABLE II

	Gas from Al Anode			Gas from Coulometer		
No.	T. V. cc	O_2 cc	H_2 cc	T.V. cc	O_2 cc	H_2 cc
1	5.0	0.2	4.8	40.0	13.3	26.6
2	5.4	0.2	5.2	50.0	16.6	33.4
3	5.8	0.1	5.7	45.0	15.0	30.0
4	10.6	0.1	10.5			

The anode was rapidly corroded as a high current density was used; and, as in the case of the magnesium, the solution became clouded with a voluminous precipitate of aluminum hydroxide of the characteristic gelatinous consistency. The evolution of hydrogen persisted for a few minutes after the electrolysis had been discontinued.

Unfortunately, electrochemical methods and efficiency measurements do not admit of the determination of the effective valence at which a metal is dissolving from the anode when the entire corrosion does not take place in accordance with that figure. When the metal has the choice of a number of possible valencies still greater are one's difficulties. This is readily seen from an illustration. If the aluminum dissolved quantitatively on the trivalent basis, stable aluminum trichloride would be formed and no hydrogen evolved. If it dissolved quantitatively to aluminum dichloride, the reaction with water could be represented thus:

$$6\,AlCl_2 + 6H_2O = 4AlCl_3 + 2Al(OH)_3 + 3H_2;$$

if to the monochloride, the equation,

$$3AlCl + 6H_2O = AlCl_3 + 2Al(OH)_3 + 3H_2,$$

would represent its reaction with water. On the above basis from the ratio of the aluminum chloride in solution or of the precipitated $Al(OH)_3$ to the hydrogen evolved could be determined readily enough whether the aluminum dissolved as the monovalent or as the divalent form. However, it is impossible to show from such analytical data, when we are not hypothesizing a quantitative corrosion as one definite electrochemical equivalent, that the corrosion has not taken place at any one of the numerous possible percentage combinations of the three valencies.

If, however, the yield of hydrogen at the anode could be shown to increase with increasing current density and could be made to approach asymptotically a certain definite value, a clue could be obtained as to the form of aluminum with which we are dealing which is not based on analogy and supposition.

The striking similarity of behavior between the magnesium and the aluminum is further instanced by the like behavior of the two in bleaching powder solution,[1] where they both dissolve with the evolution of hydrogen.

Wöhler and Buff, in an article entitled "A Compound of Silicon with Hydrogen," published some 50 years ago,[2] made note of the evolution of hydrogen at an aluminum anode. The subject has since been discussed by Norden[3] who produces evidence also from mineralogical and other sources to substantiate the hypothesis of the probable existence of aluminum of a lower valence.

Oxygen at the Cathode

The statement of Victor Meyer[4] that hydrogen, if shaken with a solution of potassium permanganate, is absorbed and that an equivalent (one-half the volume) amount of oxygen is evolved led to the belief that such a reduction with accompanying secondary reactions could be duplicated electrolytically. Accordingly, a solution of potassium permanganate, containing 5 percent by weight of $KMnO_4$ and 2.5 percent by volume of concentrated sulphuric acid, was electrolyzed

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[1] White: Loc. cit.

[2] Liebig's Ann., 103, 218 (1857).

[3] Zeit. Elektrochemie, 6, 159 (1899–1900).

[4] Meyer and Recklinghausen: Ber. chem. Ges. Berlin, 29, 2549 (1896).

between platinum electrodes in a specially constructed cell. The cell consisted of a beaker of 200 cc capacity in which, to serve as cathode compartment, was inverted a 100 cc graduated tube, drawn out at its upper end into a capillary tube and closed with rubber tubing and screw clamp. The platinum plate to serve as cathode, about 3 cm^2 on a face, was fastened to a short wire which was fused in the end of a narrow glass tube; the tube was so bent that the cathode could be projected up into the inverted, graduated tube. Connection was made with the cathode by filling the narrow tube, in which it was sealed, with mercury. To prevent the diffusion of the anode gases into the cathode compartment, the anode was carefully enclosed in a parchment envelope. Connection was then completed through a Rühstrat resistance frame and milammeter, with the storage cells. The solution was placed in the cell and drawn up into the eudiometer until it had displaced the air therein; a current was then passed until a convenient volume of gas had been collected in the eudiometer, upon which it was withdrawn into a gas burette, was measured and was analyzed for oxygen by shaking with alkaline pyrogallol in a Hempel pipette. The residue from the absorption after being subjected to qualitative tests, was in each case taken as hydrogen.

There was obtained in every case, as shown by Table III, a marked evolution of oxygen from the cathode.

Table III

Cathode Gases

No.	T.V. cc	H_2 cc	O_2 cc	Milliamps	Time, hrs.
1	42.0	29.9	12.1	125.0	1.75
2	25.6	17.9	7.7	65.0	1.5
3	26.6	19.0	7.6	25.0	5.0
4	52.0	43.5	8.5	250.0	1.0
5	50.6	42.0	8.6	1.0	18.0
6	10.8	5.0	5.8	50.0	1.5
7	12.7	7.0	5.7	50.0	1.2

The cathode became heavily encrusted with a hard and compact coating of manganese dioxide which cracked and fell off, only to be reformed. The solution, also, became thick with a black precipitate which, without analysis, was taken to be manganese dioxide.

Morse,[1] replying[2] to the paper of Meyer,[3] showed that a spontaneous decomposition of potassium permanganate occurs in solutions of this compound[4] in the presence of manganese dioxide, with an evolution of oxygen and that the reaction involved is accelerated by an increase in the amount of manganese dioxide present. With this fact in mind a number of blank experiments were run with solutions of the same concentration as above and contained in the same apparatus as that in which the electrolysis was conducted. As it was observed that the spontaneous evolution of oxygen increased up to certain limits with the age of the solution, due, no doubt, as stated by Morse, to the accumulated manganese dioxide in the solution, the blank experiments were run both before and after the experiments in which electrolysis was employed. On the basis of the average rate of evolution of oxygen thus procured were made corrections in the calculations which followed. In Table IV may be seen the results of a number of the blank experiments.

TABLE IV

No.	Time, hrs.	O_2 cc	No.	Time, hrs.	O_2 cc	No.	Time, hrs.	O_2 cc
1.0	10.0	8.0	4.0	12.0	2.5	7.0	36.0	13.0
2.0	12.0	9.0	5.0	48.0	34.0	8.0	24.0	10.0
3.0	24.0	18.0	6.0	36.0	21.0	9.0	42.0	27.0

If corrections are applied to the values shown in Table III on the basis of the figures in Table IV it is evident that the

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[1] Morse, Hopkins and Walker: Am. Chem. Jour., **18**, 401 (1896).

[2] Ber. chem. Ges. Berlin, **30**, 48 (1897).

[3] Loc. cit.

[4] Cf. Thénard: Comptes rendus, **42**, 382 (1856).

evolution of hydrogen at the cathode has been greatly accelerated by the electrolysis.

When a solution similar to that used in the above experiments was electrolyzed in a single-arm gas coulometer, the anode and cathode gases being caught together, the following figures were obtained which show that the yield of hydrogen was practically nil, or as shown by Meyer, and also by Jones,[1] which seems more probable, that the hydrogen was absorbed by the permanganate. Yet more probable does it seem that the reduction in the evolution of hydrogen from the cathode is a matter explainable by the proximity of the anode to the cathode, the oxygen there evolved acting possibly as a depolarizer at the cathode.

TABLE V

No.	T. V. cc	H_2 cc	O_2 cc	No.	T. V. cc	H_2 cc	O_2 cc
1	15.6	1.0	14.6	5	12.8	1.5	11.3
2	4.4	1.4	3.0	6	17.6	1.2	16.4
3	10.0	1.0	9.0	7	17.4	1.5	15.9
4	5.8	0.3	5.5	8	17.2	1.0	16.0

To determine the cathode efficiency in hydrogen and oxygen, so that a ratio could be obtained between the oxygen evolved at the cathode and the hydrogen which failed to be evolved, an "oxy-hydrogen gas" coulometer, filled with dilute sulphuric acid, was placed in the circuit in series with the electrolytic cell. A number of these results, chosen at random from a large number obtained, are given in Table VI.

The ratios, however, obtained on the following basis, varied widely; the results could not be duplicated even though all the conditions within one's control were maintained constant.

In attempting to explain the anomaly of the evolution of oxygen from the cathode the hypothesis of a secondary reaction, from analogy within such cases, was adopted. And

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[1] Jour. Chem. Soc., 33, 95 (1878).

TABLE VI

Cathode Gases from MnO_4				Gases from Coulometer			Ratio of oxygen evolved to hydrogen absorbed (on basis $O_2 = 2H_2$) approximate	
No.	T. V.	H_2	O_2	T. V.	H_2	O_2		
1	15.0	10.0	5.0	75.0	50.0	25.0	10:40	1:4
2	16.2	10.4	5.8	40.0	26.7	13.3	12:16	3:4
3	22.6	15.6	7.0	42.0	28.0	14.0	14:13	1:1
4	23.2	16.7	6.5	40.0	26.7	13.3	13:10	1:1
5	24.2	19.2	5.0	60.0	40.0	20.0	10:21	1:2
6	9.6	8.1	1.5	41.0	27.3	13.7	3:19	1:6
7	16.8	13.2	3.6	50.0	33.4	16.6	7:10	2:3
8	17.8	14.6	3.2	39.0	26.0	13.0	6:12	1:2
9	20.4	17.2	3.2	41.0	27.3	13.8	6:10	1:2
10	15.8	14.0	1.8	28.0	18.7	9.3	4:50	4:5
11	14.0	10.0	4.0	35.6	23.8	11.8	8:14	4:7
12	24.2	20.3	3.9	45.0	30.0	15.0	8:10	4:5
13	18.3	14.2	4.1	40.0	26.7	13.3	8:12	2:3
14	7.5	5.5	2.0	40.0	26.7	13.3	4:21	1:5
15	12.8	11.4	1.4	40.0	26.7	13.3	3:15	1:5
16	11.6	10.8	0.8	40.0	26.7	13.3	2:16	1:8
17	17.0	13.4	3.4	40.0	26.7	13.3	7:13	1:2
18	18.4	14.8	3.6	40.0	26.7	13.3	7:12	1:2

in the remaining pages will be given, as briefly as possible, a description of the experiments performed with the views which led to their performance, in our attempts to arrive at an understanding of the underlying chemistry of the electrolytic reductions of potassium permanganate. Morse[1] explained the catalytic action of manganese dioxide on potassium permanganate on the ground that the former behaves as a carrier of oxygen. In substantiation, he showed by analysis that manganese dioxide on standing in air lost oxygen and on being replaced in a solution of potassium permanganate regained oxygen. To use this fact as an explanation of our observations, the acceleration of the cathode reaction by the current must be due to the formation of a particularly reactive form of manganese dioxide, MnO_2, which was oxidized by the Mn_2O_7 to a higher, instable oxide, as Mn_2O_8, this at

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[1] Loc. cit.

once breaking down with the evolution of oxygen. Such a reactive form of MnO_2 might be a soluble form of tetravalent manganese as $Mn(SO_4)_2$,[1] a substance prepared chemically by reducing potassium permanganate with manganous sulphate, and stable only in strongly acid solutions, hydrolyzing to manganese dioxide in weakly acid solutions. No proof could be adduced, however, of a reaction between the MnO_2 and Mn_2O_7 by adding the one to the other, as the concentrated acid necessary to hold the tetravalent manganese in solution was sufficiently strong to cause alone a slow evolution of oxygen from the heptavalent manganese. The two substances were then brought together in an oxidation-reduction cell, constructed as follows:

Two small porous cups were filled respectively with a solution of potassium permanganate containing 5 percent by weight of $KMnO_4$ and 15 percent by volume of concentrated H_2SO_4 and a solution of $Mn(SO_4)_2$. Each was tightly closed by means of a two-holed rubber stopper. Through one hole in each stopper projected a glass tube through which, by means of a platinum wire sealed in its end, connection was made with a wide coiled platinum foil electrode. Through the other hole a capillary tube led from the interior of the cup to a eudiometer dipping beneath water. The two cups were then placed in a vessel filled with 15 percent concentrated sulphuric acid. The electrical circuit was completed outside the cell through a millivoltmeter. The course of the current through the external circuit was from the potassium permanganate compartment to that occupied by the manganese disulphate. The electromotive force generated produced a difference of potential between the poles of the cell of 0.1 volt.

If MnO_2 reduced Mn_2O_7, according to our hypothesis, Mn_2O_6 should be the point of equilibrium between the two. Then in the cathode compartment of the cell we should have a reduction as represented by the equation,

$$Mn_2O_7 + 2H_2 = Mn_2O_5 + 2H_2O,$$

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[1] Zeit. Elektrochemie, 11, 853 (1905).

occurring; and in the other compartment, the oxidation, as represented thus,

$$2Mn_2O_4 + O_2 = 2Mn_2O_5.$$

As is represented by these equations, the oxygen consumed at one pole is equivalent to the hydrogen consumed at the other pole. We then have formulated per equivalent of electricity one part of Mn_2O_5 by the reduction and two parts by the oxidation. From the decomposition of the Mn_2O_6 to Mn_2O_4, we should then have evolved from the cathode compartment one volume of oxygen to two volumes from the anode compartment.

From the relative amounts of oxygen evolved from the two poles, however, no evidence could be obtained to show the occurrence of a reaction between the two manganese compounds.

The reduction of Mn_2O_7 by electrolysis directly to the instable Mn_2O_5 would account for the presence of oxygen in the cathode gases. Numerous arguments for the existence of pentavalent manganese can be found in the periodic system. The proximity of this element to chlorine, and bromine, etc., would lead one to expect the existence of Mn_2O_5, analogous to Cl_2O_5 and Br_2O_5, less stable than Mn_2O_7 just as Cl_2O_6 is less stable than Cl_2O_7. Four molecules of hydrogen would reduce two molecules of Mn_2O_7 to Mn_2O_5, according to the equation,

$$2Mn_2O_7 + 4H_2 = 2Mn_2O_5 + 4H_2O$$
$$2Mn_2O_5 = 2Mn_2O_4 + O_2$$
$$2H_2 : O_2 = 2 : 1.$$

Two molecules of Mn_2O_5 breaking down to Mn_2O_4 would evolve one molecule of oxygen, making the ratio of oxygen evolved to hydrogen absorbed 1:2, a ratio frequently obtained experimentally.

The reduction of Mn_2O_7 to Mn_2O_6 and the subsequent decomposition of this oxide to the dioxide, according to the equations,

$$Mn_2O_7 + H_2 = Mn_2O_6 + H_2O$$
$$Mn_2O_6 = Mn_2O_4 + O_2$$
$$2H_2 : O_2 = 1 : 2$$

would yield a ratio of oxygen evolved to hydrogen absorbed of 2 : 1, a ratio in no instance realized experimentally. Besides no reaction between manganate and permanganate could be found in which oxygen is evolved; the decomposition of manganates results in the formation of manganese dioxide and permanganate, as shown by the equation,

$$3Mn_2O_6 = Mn_2O_4 + 2Mn_2O_7$$

an irreversible reaction in acid solution, the manganese dioxide precipitating and the reaction therefore running to an end. With the tetravalent manganese present in a soluble form as $Mn(SO_4)_2$, the reaction should be reversible.

The cathode conditions in the electrolysis were probably favorable to the production of manganates as the solution in direct contact with the cathode was no doubt alkaline from the formation there of KOH. The enveloping coat of manganese dioxide, playing the rôle of a diaphragm, would admit of slow diffusion of a manganate into the outer solution of acid permanganate. However, when these conditions were duplicated as closely as possible chemically and mechanically, no evolution of oxygen could be obtained.

Thus were practically eliminated, assuming the accuracy of our observations, the hypothesis of a reduction by MnO_2 capable of an acceleration by the electrolysis and of a direct reduction of Mn_2O_7, at the cathode to either Mn_2O_5 or Mn_2O_6.

It now seemed evident that the elusive reaction must be a function of the diaphragm formed by the heavy, compact coat of manganese dioxide enveloping the cathode. The complications incident thereto were accordingly eliminated by the use of a rapidly rotating cathode.

The cathode was attached to a rotating device.[1] Its stem projected through a mercury seal into a porous cup. The cup was tightly closed with a rubber stopper containing three holes. Through a central hole projected a glass tube through which worked the shaft of the rotating cathode; surrounding this tube was the annular shaped, mercury cup

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[1] Cf. Löb: Zeit. Elektrochemie, 7, 118 (1900).

formed from a glass tube of larger diameter, supported by a closely fitting rubber stopper and blown out at its upper end into a hemisphere with inturning edges. Dipping into the mercury cup from above was another glass tube sealed at its upper end to the stem of the cathode. By this means the cathode was allowed to rotate freely through an air-tight, mercury joint, capable of withstanding any pressure depending on the height of the mercury column. Through a second hole in the stopper projected a glass tube for introducing solutions into the cup, bearing a stop-cock and, on its upper end, a thistle-top funnel. Connection was made through the third hole by means of a capillary tube with a eudiometer. As anode was employed a broad platinum plate surrounding the porous cup. A gas coulometer was joined in series and after the cell had been partially filled with sulphuric acid of the desired strength, the current was turned on, with cathode rotating, to test the tightness of the cathode compartment. The required amount of potassium permanganate in saturated solution was then added through the funnel tube in sufficient amount to bring the concentration of the cathode solution up to the desired point and the electrolysis was continued.

With rotating cathode which precluded the possibility of the formation of a coating of manganese dioxide, even at high current densities no gas was evolved, showing a quantitative reduction of the permanganate to a stable form. Manganese dioxide was formed as before. With stationary cathode, under the same conditions of current density, gas was evolved, thus establishing the correctness of the hypothesis that the manganese dioxide diaphragm was responsible in some way for the anomalous evolution of oxygen from the cathode. It seemed quite possible that the manganese dioxide diaphragm might act like a bipolar electrode; but when this paper was presented at the May meeting of the American Electrochemical Society, Mr. F. A. Lidbury suggested that hydrogen peroxide might be formed by the electrolytic reduction of manganese dioxide. This hydrogen peroxide would be unstable and would evolve oxygen. Subsequent experiments by Mr. Wilkinson have shown that the explanation offered by Mr. Lidbury is the correct one.

At various times during the work with $KMnO_4$ the odor of ozone was noticed. This odor being particularly strong in the gas from the enclosed cathode compartment used in the last experiment, a sample of this gas was subjected to qualitative tests for ozone by the method of Keiser and McMaster.[1] Potassium iodide was instantly oxidized by it. The absence of peroxides which could scarcely be evolved from a solution of $KMnO_4$ was demonstrated by the non-appearance of a blue color on bubbling the gas through a solution of potassium ferricyanide and ferric chloride.

This work was suggested by Professor Bancroft. Its completion was made possible amid numerous distractions only by his constant interest and assistance. The author takes this opportunity of expressing to him his thanks and appreciation.

Cornell University,
April, 1908.

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[1] Am. Chem. Jour., 39, 96 (1908).

PRODUCTION OF HYDROGEN PEROXIDE FROM ALUMINUM AND ZINC

BY H. T. BARNES AND G. W. SHEARER

In a paper on "A Hydrogen Peroxide Cell" recently published by us in this Journal,[1] we have described the production of hydrogen peroxide in measurable quantities in pure water, containing clean aluminum metal, in which air or oxygen was dissolved. Keeping the water charged with air by bubbling or shaking causes a marked increase in the yield of peroxide.

At the end of our paper we state that similar experiments for zinc had yielded negative results.

Since this paper was published, however, we have repeated the experiments in a different way and have obtained considerable quantities of the peroxide. The failure of our previous tests was due to using the zinc in a powder and allowing the water to stand too long in contact.

We find that the peroxide is decomposed fairly rapidly by standing with zinc, whereas, with aluminum the peroxide is only slowly decomposed, if at all.

Clean granulated zinc in pure distilled water through which air is passed, develops considerable peroxide, but on standing, the peroxide is all decomposed in from 7 to 8 hours.

The slow action of the aluminum in decomposing the peroxide is probably due to the surface film which forms and protects the metal. In the case of zinc this surface film does not seem to be so protective, the hydroxide being more readily detached. We have tried also, copper, platinum and iron in a similar way, but up to the present have not detected free peroxide in the water. Magnesium metal gives a faint reaction for peroxide, and we believe that it is probable all the metals which show anomalous anodic conductivity are likely to develop free peroxide.

McGill University,
May 21, 1908.

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[1] Jour. Phys. Chem., 12, 155 (1908).

NEW BOOKS

Medico-Physical Works. *By John Mayow. Being a translation of Tractatus Quinque Medico-Physici. 12 × 19 cm; pp. xxiii + 331. Chicago: The University of Chicago Press, 1908. Price: $1.36.*—This volume contains all of John Mayow's papers, translated into English. Mayow was born in London in 1643 and died in 1679. In 1668 he published two papers, entitled "On Respiration" and "On Rickets." In 1674 he published three more papers, entitled "On Sal Nitrum and Nitro-aërial Spirit," "On the Respiration of the Foetus in the Uterus and in the Egg," and "On Muscular Motion." The paper on nitre is one of especial interest to the chemist because Mayow had a remarkably clear idea of the properties of oxygen more than a century before this gas was discovered officially. It is quite possible that Mayow himself would have discovered oxygen if he had not died at the age of thirty-six.

The following passages will illustrate Mayow's method of reasoning.

"But although the spirit of nitre does not proceed altogether from the air, still we must believe that some part of it originates from the air. For, since some part of the nitre is derived from the air, as has been shown above, while the fixed salt, of which nitre in part consists, proceeds from the earth, the remainder of the nitre, that is to say, its acid and fiery spirit, must be derived, in part at least, from the air. But in order that the aërial part of the spirit of nitre may be better understood, we must briefly premise the following.

"First, it is, I think to be admitted that something aërial, whatever it may be, is necessary to the production of any flame—a fact which the experiments of Boyle have placed beyond doubt, since it is established by these experiments that a lighted lamp goes out much sooner in a glass that contains no air than it does in the same filled with air—a clear proof that the flame enclosed in the glass goes out, not so much because it is choked, as some have supposed, by its own soot, as because it is deprived of its aërial food."......

"Since this treatise was written, Boyle's experiments recently published have come into our hands. In the second of these it is shown that when gunpowder is kindled, by means of a burning-glass, in a glass freed from air, the flame is not propagated, as in other cases, through the whole of its mass, but that only those grains on which the collected solar rays fall take fire. So that it appears that the access of air is necessary even for the kindling of gunpowder. I reply that although that powder will deflagrate by means of the igneo-aërial particles residing in it, in a place where there is no air, and under water, still the access of external air contributes in no small degree to its kindling. For it is to be noted that air, on account of its great elastic power, lies in the closest proximity to the sulphureous particles of the gunpowder and even presses powerfully against them, whence it is that when the powder is once ignited in free air nitro-aërial particles of the air are never lacking to keep up the flame; while, *on the other hand, the igneo-aërial particles in gunpowder are intimately* blended with the sulphureous particles only in the individual grains, and are not carried to those that are kindled; so that the flame of the powder is speedily extinguished in a vacuum owing to a break in the continuity of the igneo-nitrous particles. But how greatly the elasticity of the air helps to produce fire will be more fully established by what will be said below.

"From what has been already said, it is, I think, to some extent proved that nitre contains in itself the igneo-aërial particles required for the production of flame. Wherefore, since some part of nitre is derived from the air and igneo-aërial particles exist in it, it seems we should affirm the proposition that the aërial part of nitre is nothing else than its igneo-aërial particles.

"But now since the aërial part of nitre exists in its acid spirit, but not in the fixed salt, which, as we have already shown, forms the rest of the nitre, we may conclude that the igneo-aërial particles of nitre, which are identical with its aërial part, are hidden in the spirit of nitre, and constitute its aërial part.

"Indeed, it is probable that the spirit of nitre is a compound, and that some of its particles are flexile, humid, and of a grosser nature, being apparently derived from terrestrial matter—as I shall endeavour to show below—but that other particles are rigid, dry, and extremely subtle, agile, ethereal, and really igneous, and yet, being united with saline particles in a fluid and moist condition, are unfitted for entering on a fiery movement, and that these at any rate are derived from the air.

"With regard to the aërial part of nitrous spirit, we maintain that it is nothing else than the igneo-aërial particles which are quite necessary for the production of any flame. Wherefore, let me henceforth call the fiery particles, which occur also in air, nitro-aërial particles or nitro-aërial spirit."

"But we can perceive in the following way the extent to which the air enclosed in the glass undergoes contraction before it becomes unsuitable for sustaining animal life. For let the space in the glass occupied by the air when the animal was at first placed in it and also the space occupied by the same air when the water has risen in the glass after the suffocation of the animal be measured, as can be done by pouring water into those spaces so as to fill them and measuring it—but warning should be given here in passing that when these spaces are thus measured everything should remain in the glass the same as before. And now let it be ascertained by calculation how much the first space is greater than the second. For to that extent the air is lessened as to its elastic force and volume by the breathing of the animal. And in fact I have ascertained from experiments with various animals that the air is reduced in volume by about one-fourteenth by the breathing of the animals. But care should be taken in making this experiment that the animal be placed only a little above the surface of the water, for a reason to be afterwards given.

"From what has been said it is quite certain that animals in breathing draw from the air certain vital particles which are also elastic. So that there should be no doubt at all now that an aërial something absolutely necessary to life enters the blood of animals by means of respiration. And indeed if the necessity of breathing arose, as some have imagined, merely from this that the mass of the blood should be churned and divided into the most minute parts by the movement of the lungs, there would certainly be no reason why an animal, enclosed in a glass vessel in the manner described, should die so soon, because the air there avails as much after the death of the animal as before to inflate the lungs and consequently to churn the mass of the blood. For as that air is impelled by the pressure of nearly the whole atmosphere, there is nothing to hinder it from being urged into the dilated thorax of the animal, and on this inflation of the lungs depends, as we have shown elsewhere."

"Hence it is manifest that air is deprived of its elastic force by the breathing of animals very much in the same way as by the burning of flame. And indeed we must believe that animals and fire draw particles of the same kind from the air, and is further confirmed by the following experiment.

"For let any animal be enclosed in a glass vessel along with a lamp, so that the entrance of air from without is prevented, which is easily done if the orifice of the inverted glass be immersed in water in the manner already described. When this is done we shall soon see the lamp go out and the animal will not long survive the fatal torch. For I have ascertained by experiment that an animal enclosed in a glass vessel along with a lamp will not breathe much longer than half the time it would otherwise have lived."......

"To this I add, lastly, that air interspersed with water is drawn in by fishes for respiratory purposes. And indeed the gills with which fishes are endowed seem to be formed for this very end, that air (which is absolutely necessary for animal life) may be separated from the water by their action and mixed most intimately with the mass of the blood. And the reason that fishes are always engaged in alternately drawing in and expelling water, as terrestrial animals do common air, is that something aërial which is necessary to life may be separated from the water, as in the other case from the air, and passed into the mass of the blood.

"It corroborates this view that most fishes possess a swimming-bladder filled with air. For there can be no doubt that fishes draw this air from the pores of the water. Let me say also in passing that if a fish is placed in water contained in a suitable vessel from which the air is exhausted, it will no longer swim on its belly, but on the contrary on its back. Its belly will also rise to some extent above the surface of the water. And the reason seems to be that the air enclosed in the swimming-bladder expands in virtue of its elastic force as soon as the pressure of the external air is withdrawn, so that the said bladder and also the abdominal cavity in which it lies are inflated by the air, with the result that these swollen parts are forced upwards by the pressure of the water while the back of the fish descends. But if after the fish has died for want of air, external air is again admitted into the glass, the fish will immediately sink to the bottom and its belly will again become flaccid."

Considering this paper from our present point of view, it seems as though Mayow had discovered oxygen to all intents and purposes except that he did not prepare it pure. From the point of view of Mayow's contemporaries, it is clear that no discovery at all had been made. So far as one can learn, the paper was entirely forgotten until after the actual discovery of oxygen more than a century later. There does not seem to be any reason to believe that Mayow is the only man to have such an experience. In fact, the case of Grotthuss and the electrochemical theory of light is practically identical. The moral would seem to be that it behooves us to study the literature of the past in order to find out betimes what is to be discovered in the future. *Wilder D. Bancroft.*

Allgemeine Chemie der Kolloide. *By Arthur Müller. (Handbuch der angewandten physikalischen Chemie. Herausgegeben von G. Bredig. Band VIII.) 16 × 24 cm; pp. x + 204. Leipzig: Johann Ambrosius Barth, 1907. Price: paper, 9 marks; bound, 10 marks.*—The subject is presented under the following heads: methods of preparing inorganic colloids; organic colloids; properties of colloidal solutions; colloidal gels; theories of colloids; systematic classification of colloids. The author has done his work very well. He has gathered together a mass of data and he has arranged these data as well as could be expected in view of the rather unsatisfactory state of our knowledge of colloids. In a few cases it seems to the reviewer that a slight change in order would have improved matters. It would have been less dramatic but more effective to have treated the effects of hydrolysis and of absorption, p. 51, before the discussion of the effect of valency on precipitation, p. 48. This would have practically eliminated Whetham's calculations; but the reader would have obtained a clearer idea of the facts. In a similar way it would have been clearer to have given the method of making a hydrosol by peptization of the gel, p. 8, in immediate connection with the methods involving hydrolysis, p. 5.

In the chapter on theories of colloids the author has given a full and very fair statement of all the different hypotheses and he deserves great credit for this. In his desire to be fair he has perhaps over-emphasized the distinctive features of the different points of view. Thus we get the adsorption theory of van Bemmelen, p. 158, apparently as an alternative hypothesis to the suspension theory of Hardy and of Bredig, p. 148. In reality the two are not contradictory at all. Van Bemmelen studied the pressure-temperature concentration relations and was not especially interested in the electrical phenomena. Hardy and Bredig were especially interested in the electrical tranference and in the question of the so-called isoelectric point. It is a case of an attack on two different parts of the problem and not of two antagonistic views between which one must choose.

It is a curious fact that not one of the many theories cited by the author touches the one fundamental point in regard to colloids, the question of irreversibility. The modern theories of chemistry do not recognize the theoretical existence of irreversible phenomena, and yet we certainly appear to have such phenomena in the case of colloids. Take the dehydration of colloidal ferric hydroxide as studied by van Bemmelen. At different stages we certainly have a reversible dehydration. At other stages we apparently have an irreversible dehydration. All the experimental evidence thus far obtained points to the existence of irreversible processes. Either it must be shown that these processes are really reversible or we must develop a theory of irreversible processes. It is not enough to say that "molecular modifications take place" because that does not explain why these changes should not be reversible.

This book gives a valuable summary of much of the work on colloids and should prove the starting-point for a number of investigations.

Wilder D. Bancroft.

ON THE DISSOCIATION OF SOLUTIONS OF THE "BASIC" CASEINATES OF SODIUM AND AMMONIUM.

BY T. BRAILSFORD ROBERTSON.

(From the Rudolph Spreckels Physiological Laboratory of the University of California.)

In a previous paper[1] I have shown, from conductivity data, that the neutral caseinates of sodium and ammonium obey Ostwald's dilution-law for the salt of a monobasic acid. In this I propose to show that from the results of Sackur,[2] to which I inadvertently omitted to refer in my previous paper, it follows that the "basic caseinates" (alkaline to litmus but neutral to phenolphthalein)[3] obey the same law.

The law, as formulated in my previous paper, is as follows:

$$m = \frac{\lambda}{U + v} + \frac{\lambda^2}{G(U + v)^2} \qquad (1)$$

where m is the concentration of OH^- which has been neutralized by the casein, U is the specific ionic velocity of the cation of the base which is combined with the casein (in Cm-sec), v is that of the protein anion, $\lambda = 1.037 \times 10^{-2}\, x$, where x is the conductivity of the solution in reciprocal ohms, and G is the dissociation-constant of the salt; it is easily shown that this is identical with Ostwald's dilution-law for a binary electrolyte.[4]

Sackur's procedure was as follows: to a given amount of casein sufficient alkali was added to render the resulting

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[1] T. Brailsford Robertson: Jour. Phys. Chem., 11, 542 (1907).

[2] O. Sackur: Zeit. phys. Chem., 41, 672 (1902). I am indebted to Mr. Wm. Sutherland for having in a private letter recalled Sackur's results to my attention.

[3] Cf. van Slyke and Hart: Am. Chem. Jour., 33, 461 (1905). T. Brailsford Robertson: Jour. Biol. Chem., 2, 328, etc. (1907).

[4] Page 545 of my previous paper.

solution exactly neutral to phenolphthalein, this solution was diluted and the conductivity measured at each dilution. Since the proportion of alkali to casein which is required to secure a solution neutral to phenolphthalein is the same, within wide limits, whatever the dilution of the alkali,[1] it follows that in all these solutions the OH^- concentration was the same, namely, about 10^{-5}.[2] The procedure was, therefore, identical with that adopted by me in the experiments described in my previous paper, save that I was working with solutions which were neutral to litmus, hence, my solutions contained less sodium (or ammonium) than Sackur's in the proportion of 5 to 8.[3]

Sackur's results with "basic" sodium caseinate were as follows:

TABLE I

Concentration of solution (in equivalent sodium)	x = conductivity in reciprocal ohms.
250×10^{-4}	1160×10^{-6}
125×10^{-4}	641×10^{-6}
63×10^{-4}	351×10^{-6}
31×10^{-4}	197×10^{-6}
16×10^{-4}	109×10^{-6}

His results with "basic" ammonium caseinate were as follows:

TABLE II

Concentration of solution (in equivalent ammonium)	x = conductivity in reciprocal ohms.
180×10^{-4}	1070×10^{-6}
90×10^{-4}	590×10^{-6}
45×10^{-4}	321×10^{-6}
23×10^{-4}	173×10^{-6}
11×10^{-4}	91×10^{-6}

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[1] Van Slyke and Hart: l. c. T. Brailsford Robertson: Jour. Biol. Chem., 2, 328, etc. (1907).

[2] Cf. Salm: Zeit. phys. Chem., 57 (1906), Heft 4.

[3] Cf. van Slyke and Hart: l. c. T. Brailsford Robertson: l. c.

Inserting the observations obtained with "basic" sodium caseinate in equation (1) and applying the method of least squares to the determination of the constants, we obtain[1]

$$m = 1520\,\lambda + 0.463 \times 10^{8}\lambda^{2}, \qquad (2)^{2}$$

where $\lambda = 1.037 \times 10^{-2}\,x$. Inserting in this equation the experimentally ascertained values of λ and calculating therefrom the corresponding theoretical values of m we obtain:

TABLE III

m (Experimental)	m (Calculated)
250×10^{-4}	250×10^{-4}
125×10^{-4}	132×10^{-4}
63×10^{-4}	62×10^{-4}
31×10^{-4}	33×10^{-4}
16×10^{-4}	18×10^{-4}

Inserting the observations obtained with "basic" ammonium caseinate in equation (1) and, as before, applying the method of least squares to the determination of the constants we obtain

$$m = 1215\,\lambda + 0.370 \times 10^{8}\lambda^{2}; \qquad (3)$$

inserting in this equation the experimentally ascertained values of λ and calculating therefrom the corresponding theoretical values of m we obtain:

TABLE IV

m (Experimental)	m (Calculated)
180×10^{-4}	181×10^{-4}
90×10^{-4}	88×10^{-4}
45×10^{-4}	44×10^{-4}
23×10^{-4}	23×10^{-4}
11×10^{-4}	11×10^{-4}

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[1] Since the concentration of free (unneutralized) hydroxyl ions in each solution is of the order of 10^{-5} while that of the neutralized base is, at its least, of the order of 10^{-3} we may, with considerably less than 1% error, consider m as being the total amount of base introduced into the solution.

[2] By a misprint in my former paper, the exponent of 10 in the second constant of equations similar to these is written —8.

The agreement in both cases is excellent and leaves very little room for doubt as to the validity of the law for these solutions. The precise interpretation which is to be placed upon these results is, however, not quite clear. Consider the equilibria in these solutions. Let the concentration of the protein anion XOH^- be represented by c while that of the sodium (or ammonium) ion is β, then, assuming that the casein under these conditions behaves essentially as a monobasic acid, we have

$$c\beta = GT, \qquad (4)$$

where G is the dissociation constant of the casein salt and T is its concentration.

Let m be the concentration of OH^- which has been neutralized by the casein, then the amount of sodium (or ammonium) which is bound by protein ($=$ T) is $m - c$, assuming that no sodium is bound in complex ions or in basic ampho-salts.

Hence,

$$c\beta = G(m - c). \qquad (5)$$

Now equating the sum of the concentrations of the negative ions to the sum of the concentrations of the positive ions, assuming that the protein cation HX^+ is only present in negligible concentration, then, since the solutions are alkaline and the hydrion concentration is therefore negligible, we have

$$\beta = c + b. \qquad (6)$$

Hence substituting in (5) we have

$$c(c + b) = G(m - c). \qquad (7)$$

Now if x be the specific conductivity of the solution in reciprocal ohms and if $\lambda = 1.037 \times 10^{-3} x$, we have

$$\lambda = U\beta + Vb + vc, \qquad (8)$$

but $\beta = c + b$ so that we have

$$c = \frac{\lambda}{U + v} - \frac{U + V}{U + v} b; \qquad (9)$$

substituting in (7) we have

$$m = \frac{\lambda}{U + v}\left(1 - \frac{U + 2V - v}{(U + v)G}b\right) + \frac{\lambda^2}{G(U + v)^2} + \frac{(U + V)(V - v)}{(U + v)^2G}b^2 \quad (10)$$

since in all these solutions b is of the order of 10^{-5}, b^2 is of the order of 10^{-10} and is negligible in comparison with m. Moreover, if we assume $U = 51 \times 10^{-5}$, $V = 196 \times 10^{-5}$[1] and the values of v and G experimentally ascertained for the neutral caseinates, namely, for sodium caseinate, 3×10^{-5} and 0.04[2] we find

$$\frac{U + 2V - v}{(U + v)^2G}b = 0.002;$$

hence, this expression is negligible in comparison with unity and equation (8) becomes

$$m = \frac{\lambda}{U + v} + \frac{\lambda^2}{G(U + v)^2} \quad (9)$$

which is identical with equation (1). Since the constants have precisely the same meaning as in equation (1) this derivation indicates that the values of the constants should be the same for the neutral as for the "basic" caseinates, but this is far from being the case; in the accompanying table the values of v and of G (velocity of the protein ion and value of the dissociation-constant) for the "basic" caseinates, deduced from the above observations, are compared with those for the neutral caseinates:

TABLE V

	v		G	
	"Basic" caseinate	Neutral caseinate	"Basic" caseinate	Neutral caseinate
Sodium caseinate.....	15.2×10^{-5}	2.6×10^{-5}	0.0499	0.0395
Ammonium caseinate.	9.1×10^{-5}	—*ve*	0.0404	0.0428

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[1] The specific ionic velocities of Na^+ and OH^- at 18° given by Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," Leipzig, 1898, S. 200, multiplied by 1.14 to bring to 25°.

[2] Cf. my previous paper.

The difference between the two sets of results is surprising, but it is less so when we consider the behavior of solutions of the neutral caseinate towards the addition of alkali. Five cc of N/10 alkali dissolves one gram of casein with the formation of a solution which is exactly neutral to litmus; on continuing to add alkali to this solution, the hydroxyl concentration changes very slowly until, when 3 cc of N/10 alkali have been added, it becomes neutral to phenolphthalein.[1] Thus if we consider in the first place, 100 cc of an N/100 solution of a neutral caseinate, by the addition of alkali, the concentration of Na in the solution has been raised by 0.006 N while that of the OH^- ions has only been raised by 0.00001 N. The solution of neutral caseinate cannot contain excess of free, undissociated casein because uncombined casein is insoluble. Hence, we should be inclined to suspect that since we are dealing with a polyvalent acid, in the solutions neutral to litmus only part of the carboxyl groups have been neutralized while, on the addition of alkali, more COOH groups are neutralized. But the facts that both the neutral and the "basic" caseinates behave towards dilution precisely as do the salts of monobasic acids and that the conductivity of the "basic" caseinates is greatly in excess of that of the neutral caseinates preclude this possibility. We are therefore driven to the conclusion that the neutral and the "basic" caseinates represent two totally different types of combination between the alkali and the casein or mixtures of constant composition of these two types. In this connection, two possibilities present themselves.

In my previous paper I pointed out that it makes no difference to the *form* of equation (1) whether we are really dealing with a sodium (or ammonium) salt of casein of the type $Na^+ + XOH^-$ or with the "ampho-salt" of the type $NaX^+ + XOH^-$. If this latter is the substance in solution, however, the sum of the velocities of the cations and anions

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[1] van Slyke and Hart: l. c. T. Brailsford Robertson: Jour. Biol. Chem., 2, 317 (1907).

$(U + v)$ is no longer the sum of the velocities of the Na^+ and protein ions but is the sum of the velocities of the NaX^+ and XOH^- ions, and since the velocity of the NaX^+ ion would not probably be considerably less than that of the Na^+ ion, the *sum* of the velocities of the two ions in the solution might possibly be less than that of the non-protein ion in combination with the casein. From the fact that $U + v$ for neutral ammonium caseinate is less than U for NH_4^+ (leading to the apparently negative value for v) it was concluded that the neutral ammonium caseinate is really the ampho-salt of ammonium, and while for neutral sodium caseinate this is probably also the case, no positive proof could be adduced since $U + v$ is, in this case, slightly greater than U for Na^+. It appears possible, therefore, that in solutions of the neutral caseinates we are dealing with the ampho-salts of the bases employed while in solutions of the "basic" caseinates we are dealing with the true salts of the bases employed; it is evident that in the formation of the ampho-salt, considerably more casein would be neutralized by a given amount of alkali than in the formation of the true salt.

The quantitative relations which are observed, however, are not satisfied by the supposition that the ampho-salt is $NaX^+ + XOH^-$ while the true salt is $Na^+ + XOH^-$, for in that case, nearly twice as much alkali would be required to form the true salt as to form the ampho-salt. If, however, we assume that the ampho-salt is

$$NaX^+ + XXOH^-$$

while the true salt is

$$Na^+ + XXOH^-$$

then from the amount of NaOH (5 cc N/10 to 1 gram) required to form the neutral salt, we find that the molecular weight of the substance HXXXOH is 2000, whence the molecular weight of the substance HXXOH would be 1340 and the amount of alkali required to neutralize 1 gram of casein to phenolphthalein would be 7.5 cc of N/10 which is very close to the experimental value.

There is, however, another possibility. It is obviously indifferent as regards the form of equation (1), whether in solutions of the neutral caseinates we are dealing with the salt $Na^+ + XXXOH^-$ or with the salt $NaX^+ + XXOH^-$ and either satisfies the quantitative relation observed between the amount of alkali required to form the neutral and that required to form the "basic" caseinates. Regarding the neutral caseinate as the ampho-salt of the base, in every solution of sodium caseinate there would be an equilibrium between the ions NaX^+ and Na^+ which, as the experimental data show, is shifted in the direction $NaX^+ \rightarrow Na^+$ by the addition of sodium hydrate to the system. Regarding the neutral caseinate as the salt of a molecule of casein which has undergone association, the equilibrium would be between the ions $XXXOH^-$ and $XXOH^-$ and would be shifted in the direction $XXXOH^- \rightarrow XXOH^-$ by alkali. Since, however, Ostwald's dilution-law for a binary electrolyte holds good, and moreover, the amount of alkali necessary to form either salt depends only upon the amount of casein present and not upon its dilution it follows that the equilibrium in question is not shifted by dilution but depends only upon the proportion between the masses of Na and of casein in the system. This is obviously a relation more to be expected if the equilibrium is of the type

$$NaX^+ + HXOH \rightleftarrows Na^+ + HXXOH$$

than if it were of the type

$$XXXOH^- + H_2O \rightleftarrows HXOH + XXOH^-;$$

this consideration, taken in conjunction with the fact that the sum of the velocities of the ions in a solution of neutral ammonium caseinate is less than the velocity of the ammonium ion is, I think, sufficient to enable us to state that the neutral caseinates probably represent "ampho-salts" of the bases combined with the casein while further addition of alkali converts the ampho-salts into true salts of the bases.

It may furthermore be pointed out that while casein is very probably a polybasic acid, yet the fact that Ostwald's dilution-law for a binary electrolyte is obeyed both by the neutral and the basic caseinates indicates that, as is frequently the case with weak polybasic acids, only one COOH group is appreciably concerned in the neutralization of bases. This is in sharp contradiction to the conclusion reached by Sackur that casein acts towards bases as a 4-basic acid. He bases this conclusion upon the empirical law enunciated by Ostwald and Walden to the effect that $\frac{\Delta_{512}-\Delta_{32}}{\Delta_{512}} = 0.15$ for 2-basic, 0.22 for 3-basic and 0.29 for 4-basic acids, where Δ_{512} is the equivalent conductivity at dilution 512 and Δ_{32} is that at dilution 32. It is to be observed, however, that Sackur did not determine the equivalent conductivities at the exact dilutions employed by Ostwald and Walden, but for Na-caseinates employed the dilutions 640 and 40 and for NH_4-caseinate employed the dilutions 890 and 55.6. The exact value of the ratio, obviously cannot be independent of the dilutions at which the equivalent conductivities are determined, and as a matter of fact, Ostwald finds that the quantity $\Delta_{1024} - \Delta_{32} = 10$ for Na salts of monobasic acids, 20 for Na salts of 2-basic acids, 30 for salts of 3-basic acids, etc.,[1] a relation which could not hold good were the relation $\frac{\Delta_1 - \Delta_2}{\Delta_1}$ = const. for the salt of an acid of given basicity true for all dilutions, even provided that Δ_1 approaches the molecular conductivity at infinite dilution. However, if by interpolation from Sackur's results for "basic" Na-caseinate, using formula (2), we calculate the values of Δ_{512} and of Δ_{32} we find that $\frac{\Delta_{512}-\Delta_{32}}{\Delta_{512}} = 0.31$, indicating a 4-basic acid. But if we similarly calculate Δ_{1024} and Δ_{32} and apply Ostwald's criterion quoted above, we find that $\Delta_{1024} - \Delta_{32} = 21.2$, indicating a dibasic acid. The two empirical equations, which we are not certain can be applied to the salts of proteins, therefore lead to mutually contradictory results while the

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[1] W. Ostwald: Zeit. phys. Chem., 1, 109 (1887) 529; 2, 901 (1888).

dilution-law which, as we have seen, does apply to solutions of the caseinates, indicates a monobasic acid. We must, I think, conclude that casein acts towards bases essentially as a monobasic acid and that empirical relations founded on measurements made upon quite different substances cannot with safety be directly applied to proteins.

Referring again to Table V, it may be pointed out that the values found for the velocity of the casein ion in solutions of the "basic" caseinates are of the same order as those found by Hardy[1] by direct observation by the boundary method, and as that estimated by myself from conductivity data,[2] for the velocity of the serum-globulin ion. It will also be observed from the values of G given in Table V, that the neutral caseinates and the "basic" caseinates are about equally dissociated and that to a fairly high degree.

Conclusions

1. In a previous paper it has been shown that solutions of the neutral caseinates (neutral to litmus) obey Ostwald's dilution-law for the salt of a monobasic acid; in this paper it is shown from Sackur's determinations, that solutions of the "basic" caseinates (neutral to phenolphthalein) obey the same law.

2. In explanation it is suggested that the neutral caseinates are "ampho-salts" of the combined base (type $NaX^+ + XXOH^-$) while the "basic" caseinates are true salts of the combined base (type $Na^+ + XXOH^-$); and that in every solution of a caseinate there is an equilibrium of the type $NaX^+ + HXOH \rightleftarrows Na^+ + HXXOH$ which is independent of the dilution and depends upon the relative proportions of the base and of the casein.

3. It is concluded that only one COOH group of the casein molecule is appreciably concerned in the neutralization of bases.

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[1] W. B. Hardy: Jour. Physiology, 33, 251 (1905).

[2] T. Brailsford Robertson: Jour. Phys. Chem., 11, 437 (1907).

4. From Sackur's results it is estimated that the velocity of the casein ion in solutions of "basic" sodium caseinate is 15.2×10^{-5} centimeters per second under a potential gradient of a volt per centimeter, while in solutions of "basic" ammonium caseinate it is estimated to be 9.1×10^{-5} Cm-sec.

5. The dissociation constants of "basic" sodium and ammonium caseinates, estimated from Sackur's determinations, are respectively 0.0499 and 0.0404.

THE ABSORPTION OF THE RADIO-ACTIVE EMANATIONS BY CHARCOAL

BY R. W. BOYLE, M.SC.

(*Communicated by Dr. H. T. Barnes*)

The experiments of Sir James Dewar in 1903 drew attention to the property possessed by the charcoal of cocoanut of absorbing gases in a remarkable degree. Since then this property has been investigated by several experimenters,[1] and has been applied by Sir William Ramsay in separating the inert gases, helium and neon from the air, and measuring the quantities in which they exist in the atmosphere. The results in the papers mentioned below may be summarized as follows:

1. The absorption of gases by cocoanut charcoal is greatly increased by lowering the temperature of the charcoal.

2. The charcoal has a greater "affinity" for some gases than for others, there being something of the nature of a selective absorption. In consequence of this property it is possible to separate from one another, in some degree, the constituents of a mixed gas. The best example of such separation is found in the work of Ramsay referred to above.

3. Of the inert gases of the argon family, argon is absorbed about the same as ordinary gases, but helium and neon in a much less degree, and helium less than neon.

4. The absorption is also influenced by the pressure of the gas in contact with charcoal, the pressure—concen-

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[1] "The Absorption and Thermal Evolution of Gases Occluded in Charcoal of Low Temperature," Dewar, Proc. Roy. Soc., Vol. LXXIV, p. 122.

"The Separation of the Most Volatile Gases from Air without Liquefaction," Dewar, Proc. Roy. Soc., Vol. LXXIV, p. 122.

"The Determination of the Amount of Neon and Helium in Atmospheric Air," Ramsay, Proc. Roy. Soc., May 24, 1905.

"The Law of Distribution in the Case in which One of the Phases Possesses Mechanical Rigidity."

"Absorption and Occlusion," Travers, Proc. Roy. Soc., July 21, 1905.

tration curves varying in a regular manner with the temperature.

It was pointed out by Professor Rutherford, in a letter to *Nature*, October 6, 1906, that this property of cocoanut charcoal holds for the radio-active emanations, and in his letter are accounts of experiments demonstrating the fact. Professor Rutherford found that a slow current of air charged with the emanations of radium, thorium, or actinium is deprived of some or all of its emanation in the passage through a tube filled with cocoanut charcoal, and for this purpose the charcoal need only be at ordinary temperature. The complete withdrawal of the emanation only takes place when the air is passed very slowly through the charcoal; if the speed is increased, the amount of emanation emerging is increased also. In another experiment Rutherford found that if a tube containing less than a gram of the charcoal is open to a vessel containing the emanation from several milligrams of radium bromide, in the course of time the emanation is absorbed by the charcoal. If some powdered willemite is mixed with the charcoal, the gradual absorption is shown by the increasing brilliancy of phosphorescence of the willemite. It is not necessary to heat or exhaust the charcoal previously, but when either is done the emanation is more rapidly absorbed. The charcoal retains the emanation at ordinary temperature, but the greater part of it is expelled by heating to a low red heat.

The phenomenon of the absorption of emanation is not only of much interest in itself, but also in the fact that it may be of use in determining directly the amount of emanation existing in any particular gas. Mr. Eve, of this laboratory, has been utilizing the method to determine the amount of radium emanation existing in the free atmosphere.

It may be noted that since the emanation, in extremely small quantity, must be mixed with some gas, there is special interest in studying the information contained in the papers of Dewar and Ramsay concerning the absorption of the inert gases of the argon family which exist in the atmosphere. The cases are analogous in that the emanations are believed to be chemically inert gases and are mixed with the containing gas in extremely small proportions, but there is the distinctive difference that the emanations decay with time while the gases of the argon family do not.

It is important to determine the laws which govern the absorption of the radioactive emanations, to know how far it depends on the speed of the containing gas through the absorbent, the temperature of the absorbent, and other conditions. An investigation of these points is the main object of this paper.

Preliminary work has been carried out with the emanations of radium and thorium.

In consequence of the delicacy of electrical tests for determining the presence of minute quantities of emanations from radio-active substances, it is possible to carry out experiments with quantities of emanation far too small for examination by chemical or other known physical methods, yet the measurements are capable of a high degree of accuracy.

Radium Emanation

A short account may be given of a few experiments on the diffusion of radium emanation from vessels containing the emanation mixed with air to vessels containing cocoanut charcoal. The apparatus used, Fig. 1, was an emanation electroscope, which consists of two chambers, one above the other. The lower chamber is an air-tight, cylindrical vessel of brass of about one liter cubical capacity, serving as an emanation reservoir, while the upper is a vessel covering the gold leaf system which can be observed through a mica window by a microscope with a scale in the eye-piece. The gold leaf is at the upper end of a brass rod which extends down into the lower chamber and is well insulated. The lower chamber is fitted with tubes and stop-cocks, through which air charged with emanation can be admitted or withdrawn at will by means of a pump. Connected with the emanation reservoir by a short tube of large cross-sectional area was a glass bulb containing a few grams of cocoanut charcoal in granulated form. The outside of the electroscope was earthed and the ionization currents measured by the rate of movement of the gold leaf. The ionization current, or activity, at any time is proportional to the amount of emanation present in the emanation reservoir.

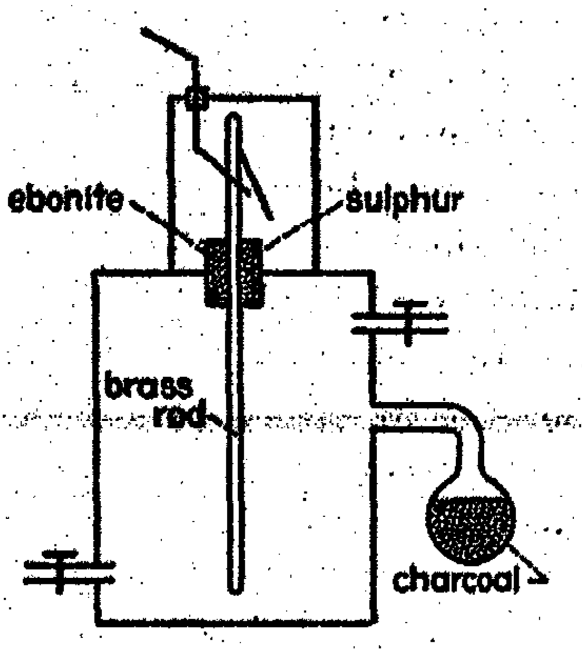

Fig. 1

When radium emanation was admitted into and retained in the electroscope, it was found that the decay of activity did not follow an exponential law, for while at the first the activity fell to half-value in 1.0 day, in the course of five or six days the rate was half-value in 1.6 or 1.7 days.

When the emanation reservoir was refilled with emanation and the charcoal vessel removed, so that the emanation could diffuse to the open air, the decay of activity did follow an exponential law, the time for diminution to half-value being 1.0 day. This result may be expected, for it means that the amount of emanation diffusing to the open air per second is proportional to the amount of emanation in the reservoir. P. Curie and Danne[1] performed experiments of this kind with capillary tubes as the communication from the emanation reservoir to the outside air, and found that the loss of emanation from the reservoir was exponential.

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[1] P. Curie and Danne: Comptes rendus, 136, p. 1314 (1903).

It should be noticed that, in these experiments, if the emanation reservoir were sealed, so that there could be no diffusion to charcoal or to open air, the activity would fall to half-value in 3.75 days.

From the figures above, the rate of diffusion of the emanation from the reservoir to the charcoal was at first the same as the rate of diffusion to the open air, *viz.*: half-value in 1.0 day; but as time went on this rate gradually became less. A probable explanation of this fact is that the layer of charcoal first reached by the emanation acts as a good absorbent until it becomes saturated, very little emanation passing to the under layers until the top layer reaches this condition. In consequence, it will take time for the emanation to diffuse from the upper to the lower layers of charcoal, with the result of a gradual lessening of the amount of emanation absorbed from the reservoir.

Another experiment was made with the emanation diffusing to a very thin layer of charcoal, and the results obtained support this explanation. In this case the activity diminished at first at the rate of half-value in 1.3 days, but kept gradually changing until, after twenty-four hours, the rate was half-value in 3.2 days. At this stage there could be very little absorption, since the natural decay of the emanation itself is half-value in 3.7 days. We may say, then, that it took about a day to saturate the thin layer of charcoal.

In the experiments just described the charcoal has been contained in a vessel outside the emanation reservoir; when the charcoal is in the reservoir itself, the absorption takes place more rapidly, as the time for the emanation to diffuse through the connecting tubes is eliminated. In an experiment where a tray containing charcoal was placed in the bottom of the emanation reservoir, on admitting some emanation the absorption took place so quickly that there was not the usual rise of activity due to the active deposit, but, on the contrary, an immediate, rapid fall. With only a thin layer of charcoal—a sprinkling covering the bottom of the tray—there is a slight rise of activity due to the active deposit, but not nearly in the same degree as if the charcoal had been absent.

The above experiments were all performed in a constant temperature room, so that all effects on the diffusion by changes of temperature and draughts of air were avoided.

More experiments, along the same lines as the above, are being carried on.

Thorium Emanation

In the case of thorium emanation, owing to its short period of decay—to half-value in 54 seconds—it is necessary to use a flow method of experiment. In other words, the emanation must be mixed with some gas, and conducted through tubes containing absorbing, or non-absorbing, material into a testing vessel, where it ionizes the air, and the ionization currents can be measured by means of an electrometer. The apparatus used for the experiments is represented by the accompanying diagram, Fig. 2.

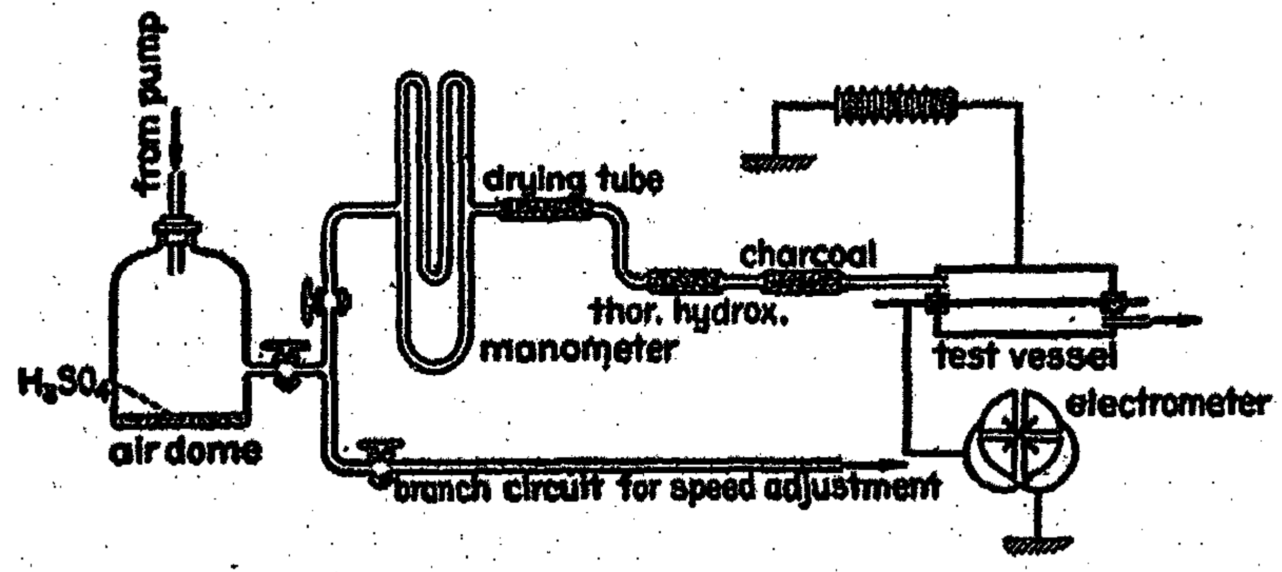

Fig. 2

An air-pump supplies a current of air through a tube of thorium hydroxide, where the emanation mixes with the air and thence passes through tubes, containing absorbing or non-absorbing material, as the case may be, into a testing vessel of the ordinary cylindrical type. An accurately calibrated manometer in the circuit measures the velocity of the air current. The testing vessel is connected to one pole of a battery of electromotive force sufficient for complete saturation, the other pole of the battery being earthed. The central rod of the testing vessel is connected with a suitable electrometer, and a condenser of adjustable capacity is placed in parallel with it. It should be noticed, that, with this arrangement, absorption of the emanation can only take place after the charcoal has absorbed its full amount of the atmospheric gases.

The weight of thorium hydroxide used was 37 grams.

Using this apparatus when there is no absorbing material between the thorium hydroxide and the testing vessel, and taking observations of the ionization current with varying speed of the air current, we get a curve such as is shown in Fig. 3 (Table 1), which has ionization currents (i) for ordinates and speeds of the air current in cubic centimeters per second (q) for abscissae. We shall hereafter call this the $i - q$ curve.

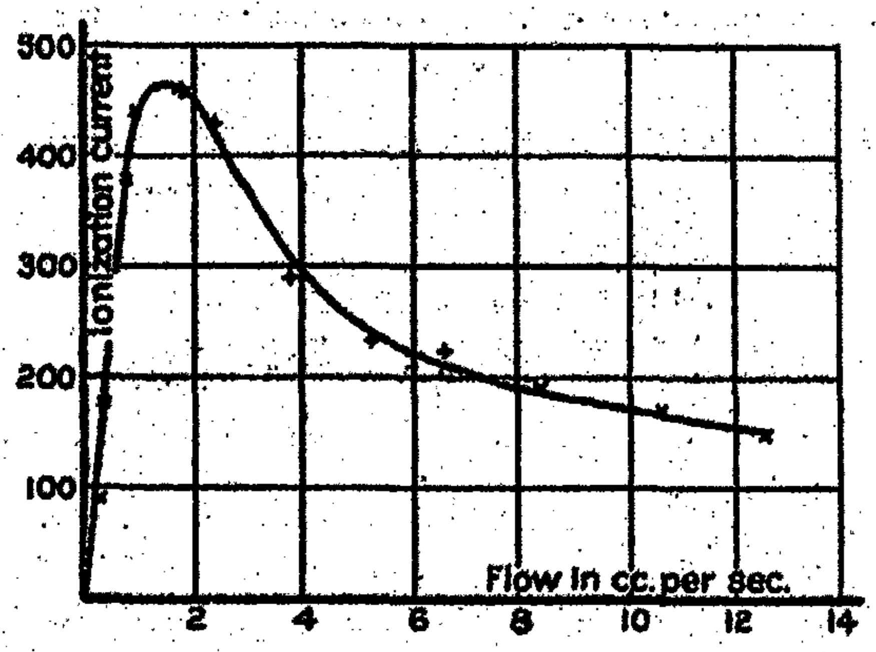

Fig. 3

The shape of this curve can be deduced from theoretical considerations by the following:

The thorium hydroxide, in radio-active equilibrium, gives off free atoms of emanation at a constant rate, and these are all removed by the air current. In consequence, there will be the same number of emanation atoms leaving the thorium tube per second for any speed of the air current.

TABLE 1—(Fig. 3)

Emanation Directly into Testing Vessel

Flow in cc/sec.	Ionization current in arbitrary units
0.30	91
0.37	174
0.76	380
1.12	441
1.86	464
2.52	438
3.80	291
5.18	238
6.60	224
8.40	192
10.70	169
12.60	149

The ionization current in the testing vessel is proportional to the number of emanation atoms breaking up per second in the testing vessel, and this number is λ times the number of emanation atoms present, λ being the coefficient of decay of the emanation.

Let N = the number of free emanation atoms given off by the thorium hydroxide per second,
q = the flow of the air current in cubic centimeter per second,
t = the time for the air to pass from the thorium hydroxide to the testing vessel.

Then with q cubic centimeter of air entering the testing vessel are associated $Ne^{-\lambda t}$ atoms of emanation. If we denote the number of emanation atoms per cubic centimeter of air at the entrance of the testing vessel by n_0,

$$\text{then } n_0 = \frac{Ne^{-\lambda t}}{q}.$$

Let V be the total free volume of the conducting tubes between the thorium hydroxide tube and the testing vessel, then $t = \frac{V}{q}$,

$$\text{and} \therefore n_0 = \frac{Ne^{-\lambda t}}{q} = \frac{Ne^{-\frac{\lambda V}{q}}}{q}.$$

To obtain the total number of emanation atoms, P, present in the testing vessel, consider an element of volume *dw*, with a volume *w* between the entrance and the element as shown by Fig. 4, $\frac{w}{q}$ is the time for the air to traverse the volume *w*, and therefore, if $n =$ the number of emanation atoms per cubic centimeter of air within the element,

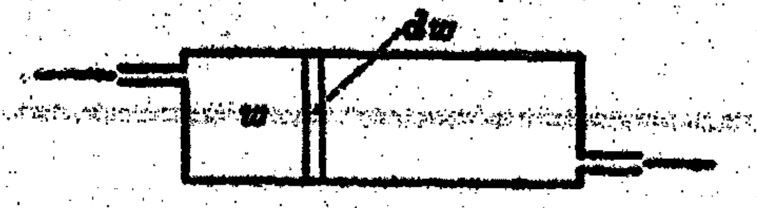

Fig. 4

$$n = n_0 e^{-\lambda \frac{w}{q}}.$$

The total number of emanation atoms in the element *dw*

$$= n\, dw$$

$$= n_0 e^{-\lambda \frac{w}{q}} dw$$

$$\therefore \mathrm{P} = \int_0^{\mathrm{W}} n_0 e^{-\lambda \frac{w}{q}} dw$$

where W is the whole volume of the testing vessel.

Integrating, we get

$$\mathrm{P} = \frac{qn_0}{\lambda}\left[1 - e^{-\lambda \frac{\mathrm{W}}{q}}\right],$$

and substituting for n_0,

$$\mathrm{P} = \frac{\mathrm{N}}{\lambda} e^{-\lambda \frac{\mathrm{V}}{q}}\left[1 - e^{-\lambda \frac{\mathrm{W}}{q}}\right].$$

The ionization current is proportional to the number of emanation atoms breaking up per second, which is λ times the number present, *i. e.*, λ P.

Hence, if i is the ionization current, $i = \mathrm{K}\,\lambda\,\mathrm{P}$, where K is a constant,

$$\text{and } \therefore i = \mathrm{K\,N}e^{-\lambda\frac{\mathrm{V}}{q}}\left[1 - e^{-\lambda\frac{\mathrm{W}}{q}}\right] \text{..........(1).}$$

If we plot a curve with ionization currents as ordinates and flow of air in cubic centimeter per second as abscissae, we can see from (1) what the shape of the curve should be.

Denoting $-\lambda\mathrm{V}$ as a, and $-\lambda\mathrm{W}$ as b, we have,

$$i = \mathrm{K\,N}\,e^{\frac{a}{q}}\left[1 - e^{\frac{b}{q}}\right],$$

from which we can at once see that $i = 0$ when $q = 0$ or ∞. Differentiating, we get

$$\frac{di}{dq} = \mathrm{K\,N}e^{\frac{a}{q}}\left[(a + b)\,e^{\frac{a}{q}} - a\right],$$

from which it follows that i is maximum when

$$q = \frac{a}{\log\frac{a}{a+b}}, \text{ or}$$

$$\text{when } q = \frac{\lambda\mathrm{V}}{\log\frac{\mathrm{V}+\mathrm{W}}{\mathrm{V}}} \text{....................(2).}$$

The curve, then, must rise from zero to a maximum, and fall off to nothing as the speed of the air current increases to infinity.

It can be seen that the curve of Fig. 3 conforms to these conditions.

The relation deduced in (1) shows us that the ionization current depends not only on q, the speed of the air current, and on W, the volume of the testing vessel, but also on V, the free volume of the space through which the emanation has to pass before it reaches the testing vessel. When V is increased i is decreased; and, following from the condition for a maximum (2), q must be increased to give the maximum ionization current. Hence it follows, that in experimenting to compare the absorption by different substances or by different quantities of the same substance, the free volume between the thorium hydroxide and the testing vessel should be constant. In the experiments described later, where it was desired to compare the absorption, care was taken to have this condition fulfilled.

When an absorbing material is inserted between the thorium hydroxide and the testing vessel, there is less emanation available for ionization and the *i* — *q* curve is much altered. In the case of charcoal, in granulated form, it has been found that the amount of absorption depends on[1]

(*a*) The nature of the charcoal,

(*b*) The speed of the air current through the absorbent,

(*c*) The amount of charcoal surface exposed to the emanation,

(*d*) The temperature of the charcoal.

In the experiments on these points, the results of which are given later, the *i* — *q* curves in the cases of non-absorption were obtained by substituting for the tube containing the charcoal a similar tube containing a non-absorbing sand of the same volume and of the same size grain as the charcoal used. This precaution was necessary in order to have the same volume between the thorium hydroxide and the testing vessel in the case of non-absorption as in the case of absorption. In all experiments with a given sample of sand or charcoal, an attempt was made to have the grains of uniform size by sifting through a set of sieves and collecting separately the residues caught in the meshes of each sieve.

(a) Nature of the absorbent

Fig. 5 (Table 2) shows the *i* — *q* curves, taken under the same experimental conditions, for the cases of absorption by ordinary wood, animal, and cocoanut charcoal, all of the same volume and same size grain. The wood charcoal weighed 0.77 gram, animal 2.25 grams, and cocoanut 2.17 grams.

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[1] "The Effect of Temperature and of Velocity of Gas Current on the Absorption of Radio-active Emanations by Charcoal," R. W. Boyle, Transactions of Royal Society of Canada, May, 1907.

TABLE 2—(Fig. 5)

Multiply currents by 617 × 10^{-15} for amperes

Non-absorption		Wood charcoal		Animal charcoal		Cocoanut charcoal	
Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current
Nat. leak at beginning	3.94	Nat. leak at beginning	0.81	Nat. leak at beginning	1.46	Nat. leak at beginning	1.63
0.40	31.6	0.53	32.7	0.37	3.48	1.07	6.24
0.63	90.8	1.07	113.9	0.60	26.8	1.48	16.9
0.93	135.8	1.52	141.0	0.97	73.0	1.89	30.08
1.33	161.1	1.95	147.0	1.34	88.4	3.07	42.8
1.83	169.9	2.37	136.4	1.67	97.1	3.47	46.1
2.34	157.7	2.84	123.2	2.38	98.0	4.15	45.7
2.74	149.1	3.62	101.7	Nat. leak at end	3.42	4.91	44.4
3.46	124.3	4.76	83.6			6.09	43.7
4.20	105.9	5.95	75.2			7.64	43.9
4.78	92.5	6.80	70.7			8.77	42.0
5.51	85.7	8.40	62.9			Nat. leak at end	2.26
7.10	78.0	Nat. leak at end	1.84				
8.66	68.5						
Nat. leak at end	5.69						

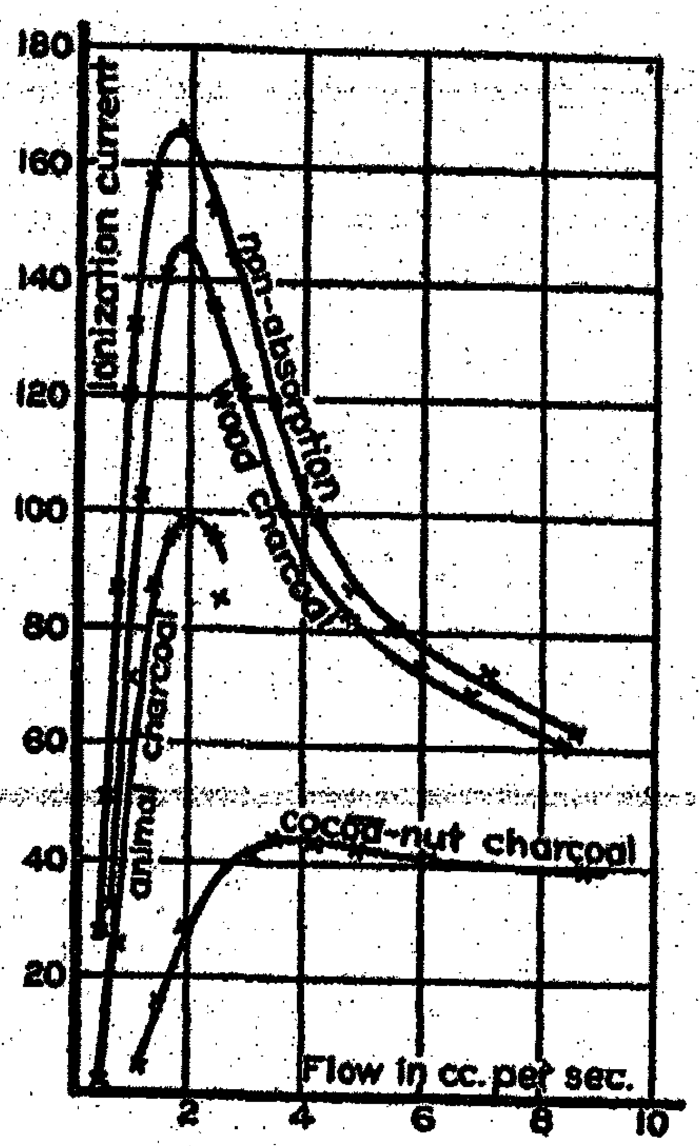

Fig. 5

The curves show that cocoanut charcoal absorbs the most and ordinary wood charcoal the least of the three, and that the variation in absorptive power is very marked. In fact two different samples of the same kind of charcoal can show appreciably different absorptive powers. I have had samples of cocoanut charcoal, taken from different lots, showing considerable difference in this respect, the better absorbers being softer, less gritty, and less dense than the others.

(b) Speed of the air current

An inspection of the curves mentioned above, or of any of those following, will show that the amount of absorption depends on the speed of the air current which conducts the emanation through the absorbent material.

The absorbent must have time to absorb and at quick speeds it does not get as good a chance.

The following facts, taken from Fig. 5 and tabulated, illustrate very well (*a*) and (*b*). Here the percentage absorption for any given speed is represented by

$$100 \times \frac{\text{Difference between non-absorption and absorption ordinates.}}{\text{Non-absorption ordinate}}$$

The table shows that the percentage absorption is increased as the speed of the air current is decreased.

Absorbent	Speed of air current	Ionization current absorption	Ionization current non-absorption	Percent absorption
Wood charcoal	0.7	55	93	40.9
	1.0	94	138	31.9
	1.5	139	164	14.8
	4.5	86	92	6.5
	8.0	63	66.5	5.3
Animal charcoal	0.5	11	55	80.0
	0.7	31.5	93	66.2
	1.0	62	138	55.0
	2.0	98.5	164	39.9
Cocoanut charcoal	1.5	16	164	90.3
	2.0	28.5	164	82.6
	4.5	43	92	53.3
	8.0	40	66.5	39.8

(c) The surface exposed to the emanation

It is natural to suppose that the amount of absorption will in some way depend on the amount of the charcoal absorbing surface, that, in fact, the absorption will be increased if the surface be increased.

To prove the point experiments were performed, the results of which are given in Table 3 and Fig. 6.

For a particle of material the ratio of its surface to its mass becomes greater when the size of the particle is reduced; hence one lot of charcoal, equal in mass to a second lot, will have a greater or less surface than the second, according as the size of its grains is smaller or larger than the size of the grains of the second.

TABLE 3—(Fig. 6)

Multiply currents by 617 × 10^{-15} for amperes

Curve I, No. 10		Curve II, No. 20		Curve III, No. 30	
Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current
Nat. leak at beginning	2.16	Nat. leak at beginning	1.07	Nat. leak at beginning	1.63
0.49	4.46	0.715	3.86	1.07	6.24
0.94	37.5	1.17	20.3	1.48	16.9
1.44	73.1	1.54	39.7	1.89	30.1
1.99	92.5	2.31	54.1	3.07	42.8
2.49	93.3	2.50	61.2	3.47	47.2
3.21	86.5	2.88	61.2	4.15	45.7
3.80	82.1	3.32	59.6	4.91	44.4
4.77	75.0	4.07	57.3	6.09	43.7
5.85	71.8	4.46	54.4	8.77	42.0
7.00	69.3	5.46	54.0	Nat. leak at end	— 2.26
8.34	64.3	6.73	52.4	—	—
Nat. leak at end	— 3.29	8.46	50.5		
		Nat. leak at end	1.34		

Non-absorption the same as given in Table 2.

In this particular experiment three equal masses, 2.17 grams, of the *same* sample of cocoanut charcoal were used, but the size of the grain was different in each case. The $i - q$ curves were taken for all four. I is the curve for the grains which were just caught in a sieve of ten meshes to the inch, II for twenty meshes to the inch, and III for thirty meshes to the inch. It can be seen that the larger the grain the less is the absorption, or, in other words, the smaller the surface the less the absorption.

The experiment shows that it is not the mass of the absorbent on which the amount of absorption depends, but rather the amount of surface which the mass exposes to the emanation.

By increasing the quantity of charcoal of a given size grain the amount of absorbing surface is also increased, and

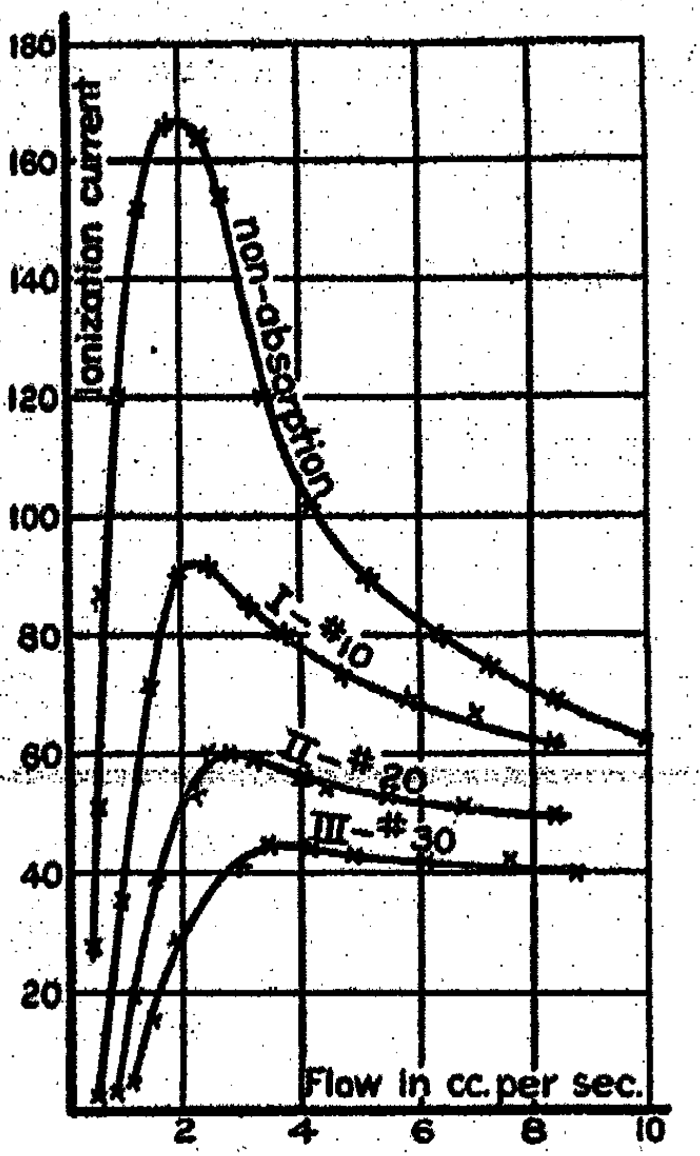

Fig. 6

consequently there is increased absorption. This is demonstrated by the results in Table 4, Fig. 7, which shows the experimental $i - q$ curves for 1.18, 2.17, and 3.35 grams of the same sample of cocoanut charcoal of the same size grain (just caught in a sieve 30 meshes to the inch).

It must be noticed that the greater the quantity of charcoal, or, for that matter, the greater the absorbing capacity by any condition, the greater must be the speed of the air current to get any effect at all in the testing vessel. Thus, up to a speed of 0.5 cc per second there is practically 100 percent absorption for 1.18 grams of charcoal, 0.8 cc per second for 2.17 grams, and 1 cc per second for 3.35 grams.

(d) The temperature of the charcoal

The experiments of Dewar showed that when cocoanut charcoal is used as an absorbent of gases, the absorption is

TABLE 4—(Fig. 7)

Multiply currents by 616 × 10^{-15} for amperes

Non-absorption		1.18 grams cocoanut charcoal		2.17 grams cocoanut charcoal		3.35 gms. cocoanut charcoal	
Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current
Nat. leak at beginning	3.94	Nat. leak at beginning	1.79	Nat. leak at beginning	1.63	Nat. leak at beginning	0.88
0.40	31.6	0.62	4.90	1.07	6.24	1.17	2.11
0.63	90.8	0.98	20.3	1.48	16.9	2.03	8.84
0.93	135.8	1.36	45.2	1.89	30.1	2.82	18.2
1.33	161.1	1.80	61.9	3.07	42.8	4.00	25.2
1.83	169.9	2.19	69.0	3.47	47.2	5.05	28.4
2.34	157.7	2.77	73.4	4.15	45.7	6.21	30.8
2.73	149.1	3.38	67.9	4.91	44.4	7.19	32.8
3.46	124.3	4.13	62.7	6.09	43.7	8.28	32.5
4.20	105.9	5.18	58.5	8.77	42.0	9.37	32.3
5.18	94.0	6.27	56.8	Nat. leak at end	2.26	Nat. leak at end	1.11
6.40	84.1	8.26	54.4				
7.32	79.4	Nat. leak at end	2.65				
8.39	73.5						
Nat. leak at end	5.69						

greatly increased by lowering the temperature of the charcoal.

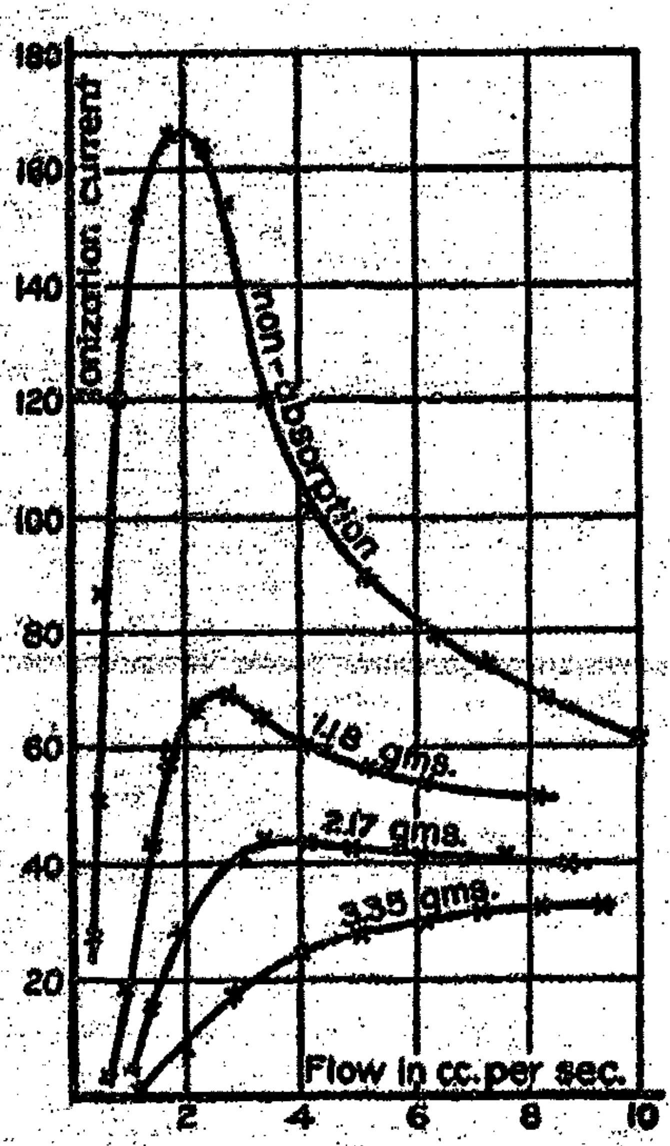

Fig. 7

The same law holds for the radio-active emanations when absorbed by any kind of charcoal. To determine the point experiments were carried out at different temperatures of samples of wood, animal, and cocoanut charcoal. The weight of charcoal used was about 1.8 grams.

Temperatures were measured by a Callendar platinum-resistance thermometer, the bulb of which was surrounded by the charcoal. The stem of the thermometer was sealed into the tube containing the charcoal by an asbestos and plaster of Paris packing, so that the joint was perfectly air-tight. The diagram, Fig. 8, shows the arrangement.

The lowest temperatures mentioned were obtained from a mixture of solid carbon dioxide and ether, those next above, *viz.*, 17.6°, 16.1°, were the temperatures of the room. The remaining were obtained by heating in a specially constructed oven so that the temperature variation was not any more than 3° or 4°.

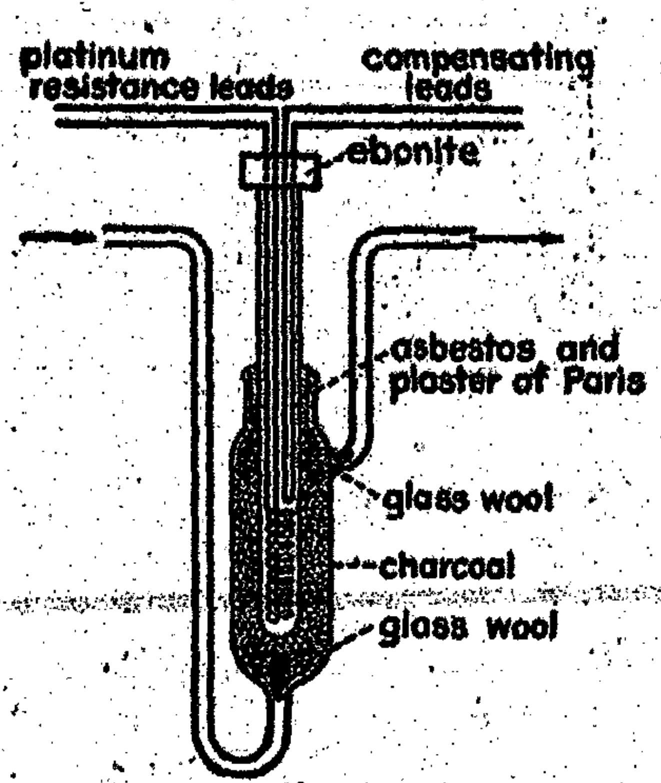

Fig. 8

For cocoanut charcoal, curves were taken at five temperatures, *viz.*, 185°, 124°, 69.5°, 17.6° and —75.5° C, Fig. 9, Table 5.

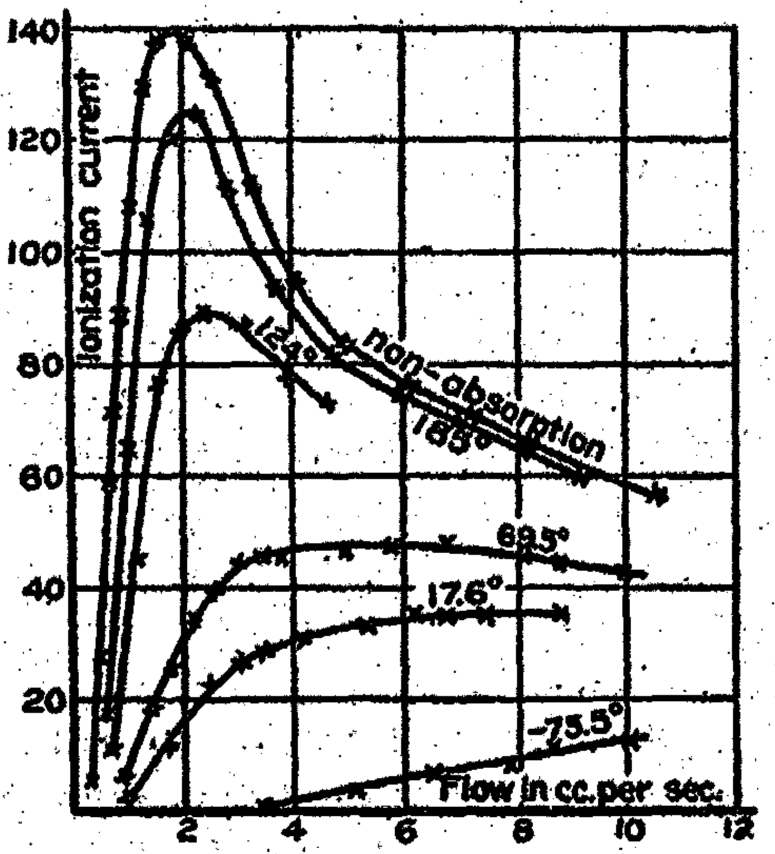

Fig. 9

TABLE 5—(Fig. 9)—COCOANUT CHARCOAL

Multiply currents by 618×10^{-15} for amperes

Non-absorption		Temperature 185° C.		Temperature 124° C.		Temperature 69.5° C.		Temperature 17.6° C.		Temperature —75.5° C.	
Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current
Nat. leak at beginning	0.93	Nat. leak at beginning	3.71	Nat. leak at beginning	0.93	Nat. leak at beginning	1.35	Nat. leak at beginning	0.86	Nat. leak at beginning	0.89
0.38	6.39	0.66	19.4	0.47	1.25	0.47	1.72	1.01	2.71	2.51	1.09
0.53	28.5	1.02	69.0	0.75	11.9	0.92	6.63	1.23	5.51	3.61	1.58
				1.11	46.1	1.44	19.7	1.76	12.4	4.07	2.82
0.71	59.4	1.44	109.5	1.59	77.6	1.83	27.1	1.87	14.6	5.17	4.54
0.92	89.6	1.88	124.1	2.04	88.9	2.18	35.5	2.51	23.4	6.51	7.56
1.10	108.9	2.33	127.7	2.42	90.3	2.59	41.0	3.06	27.3	7.82	8.44
1.36	130.0	2.87	115.0	3.19	88.4	3.02	45.9	3.51	29.8	8.68	12.00
1.58	138.2	3.77	97.8	3.90	78.9	3.50	47.2	3.84	30.9	10.08	13.23
2.10	139.1	4.77	85.2	4.72	74.7	5.04	48.4	4.82	32.5	Nat. leak at end	0.89
2.61	132.5	5.97	79.9	Nat. leak at end	3.19	5.82	49.1	5.62	34.5		
3.32	113.3	7.06	74.7			6.76	49.5	6.24	36.5		
4.08	96.2	8.13	69.3			8.12	47.3	6.76	36.2		
5.05	85.3	9.26	64.1			8.79	45.7	7.44	37.2		
6.19	78.3	Nat. leak at end	5.04			10.01	43.9	8.00	37.2		
7.17	73.4					Nat. leak at end	1.70	8.82	36.6		
8.27	68.7							Nat. leak at end	1.47		
10.54	59.6										
Nat. leak at end	3.31										

For wood charcoal, three curves were taken corresponding to 170°, 16.1° and —74.2° C, Fig. 10, Table 6.

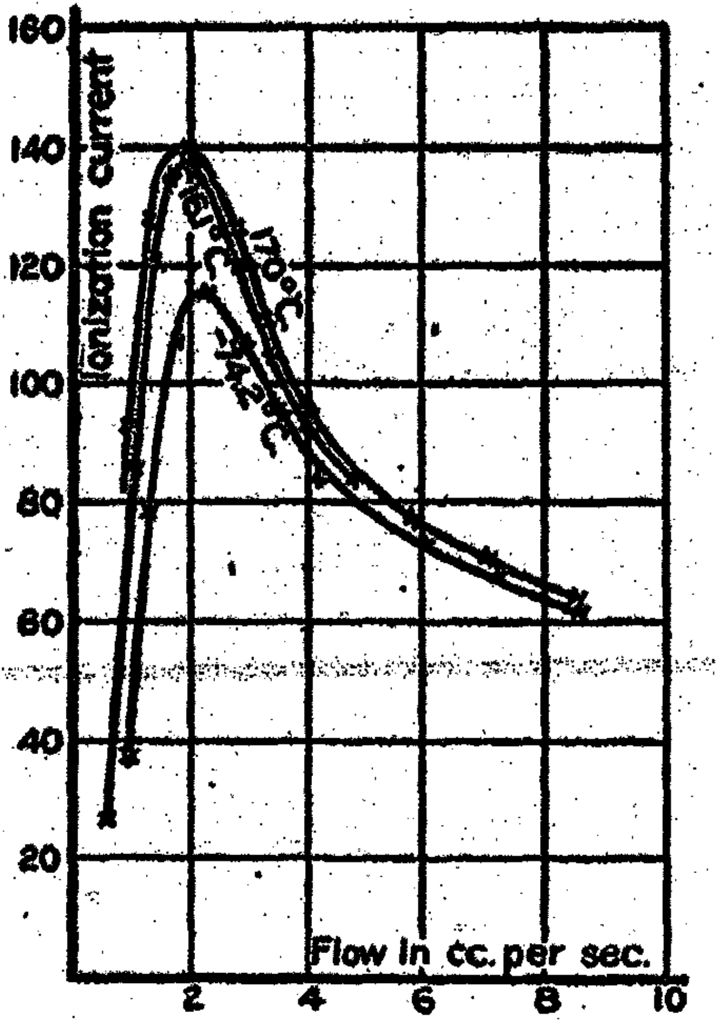

Fig. 10

TABLE 6—(Fig 10)—WOOD CHARCOAL

Multiply currents by 613 × 10^{-15} for amperes

Temperature 170° C.		Temperature 16.1° C.		Temperature —74.2° C.	
Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current	Flow in cc/sec.	Ionization current
Nat. leak at beginning	1.45	Nat leak. at beginning	3.38	Nat. leak at beginning	1.73
0.86	94.5	0.53	30.2	0.83	38.8
1.18	129.2	0.93	88.9	1.20	80.3
1.91	141.0	1.30	124.7	1.73	109.2
2.72	129.7	1.66	138.7	2.31	117.8
3.27	112.6	2.10	141.0	2.92	109.2
3.99	97.8	2.82	124.2	3.52	97.8
4.84	85.0	3.38	109.1	4.16	86.0
5.84	79.6	4.02	96.5	4.99	80.4
7.04	74.4	4.81	88.3	6.11	75.5
8.54	66.1	Nat. leak at end	4.50	7.27	70.6
Nat. leak at end	2.74			8.61	63.8
				Nat. leak at end	2.61

The curves show at once that the above law holds. Wood charcoal is not under any condition a good absorber, yet it is found to be affected by temperature according to the law. The absorption by animal charcoal is affected in a similar manner, but the results are not given here. The curve for non-absorption in the case of wood charcoal is not plotted in Fig. 10, for it is virtually the same as the curve for 170° C. At this temperature there was practically no absorption.

The following tabulated facts are taken from the curves of Figs. 9 and 10.

Wood charcoal

Speed of the air current	Percentage absorption		
	At 170° C	At 16.1° C	At −74.2° C
1.0	0 (practically)	20.6	39.2
2.0	0 "	2.14	18.3
3.0	0 "	1.47	11.0
6.0	0 "	—	3.16

Cocoanut charcoal

Speed of the air current	Percentage absorption				
	At 185° C	At 124° C	At 69.5° C	At 17.6° C	At −75.5° C
1.0	35.1	64.9	92.4	98.0	100
2.0	11.2	37.3	78.7	89.2	100
4.0	6.45	20.0	51.2	68.5	98.5
6.0	4.15	—	37.8	55.3	93.7
8.0	3.00	—	31.6	47.6	85.5

In a special experiment it was determined that the cocoanut charcoal begins to give off carbon dioxide at 211° C, yet at even higher temperatures than this it showed some power of absorbing the emanation. By using a large quantity of charcoal, and keeping the speed of the air current constant at 1.65 cc per second, it was found that the ionization current in the testing vessel kept slightly decreasing, thus showing a slight but gradually decreasing absorption, up to about

300° C, when the ionization current began to increase and soon gave the same value as in the case of non-absorption. This increase was no doubt due to the loss of charcoal by oxidization, and to the increased conductivity of the gas in the testing vessel, owing to the presence of carbon dioxide. (For α-ray ionization the conductivity of carbon dioxide is 1.5 times that of air.)

In connection with the above experiments it should be noticed that it is not possible for the charcoal to become "saturated" with thorium emanation, that is, to reach a state when it cannot occlude any more emanation, as it would in the case of ordinary gases. It must be remembered that the emanation which has been occluded by the charcoal is itself decaying at the rate of half-value in *54 seconds*.

In the observations of ionization currents given above, the numbers represent the current when it has reached a *steady* state. At slow speeds the current keeps increasing for a few minutes until it becomes steady, but at high speeds it takes a steady value almost immediately.

Conclusion

To conclude it may be said that the percentage absorption of thorium emanation by means of charcoal (1) depends on the nature of the charcoal used, being greatest for cocoanut, intermediate for animal, and least for wood charcoal; (2) is decreased by increasing the velocity of the gas current which conducts the emanation through the charcoal; (3) is increased by increasing the charcoal absorbing surface; and (4) is dependent on the temperature, following the law for ordinary gases, *viz.*, that a lowering of the temperature of the charcoal causes an increase, and a raising of the temperature, a decrease in the amount of absorption.

THE IRON-CARBON EQUILIBRIUM

BY G. B. UPTON

For over half a century the need has been felt for a rational basis of knowledge for the manufacture and preparation of iron and steel for engineering uses. Little progress was possible until the development of physical chemistry; the older chemistry was not powerful enough to solve the problem. Experiments by physico-chemical methods began about 1890 to 1895. In 1899 Professor Roberts-Austen was able to present, as the fifth report of the Alloys Research Committee of the British Institution of Mechanical Engineers,[1] the first attempt at an equilibrium diagram between iron and carbon.

The points of the diagram were found by means of differential cooling curves. Accepting Osmond's hypothesis of the allotropism of iron, Professor Roberts-Austen charted the temperature and constitution relations of iron and carbon as in Fig. 1. Little need be said concerning the diagram, as in 1900 the physical chemist Roozeboom used the same data for a thorough discussion, so far as the data would allow, and published the familiar "Roozeboom diagram."[2] This diagram, save for a slight change in the melting-point of pure iron, is shown by the lines of Fig. 2.

According to Roozeboom the phases separating from the melt are graphite and martensite, the latter a solid solution of carbon (or a carbide) in the allotropic modification of iron. Under the line of the liquid eutectic lies a two-phase field of martensite plus graphite. The solid solution becomes unstable with decreasing temperatures and breaks down. If the carbon is below 0.35 percent, carbonless β iron is formed from the solid solution. With between 0.35 and 0.90 percent carbon the phase separating from the solution is carbon-

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[1] Proc. B. I. M. E., 1899. Some cooling curve work on iron-carbon was also given in the fourth report in 1897.

[2] Zeit. phys. Chem., 34, 437 (1900).

less α iron. Above 0.9 percent carbon part of the martensite produces cementite, the chemical compound Fe_3C. The pointed lower end of the martensite field is a eutectic in the solid, exactly analogous, save for the change in physical condition, to the liquid eutectic. This eutectic of carbonless α iron (ferrite) and cementite is called pearlite. Though Roberts-Austen had little definite thermal evidence of an inversion from martensite plus graphite to martensite plus cementite, Roozeboom found such an inversion theoretically necessary and placed it provisionally at a temperature of 1000° C. This completes the listing of the phases and fields of the Roozeboom diagram.

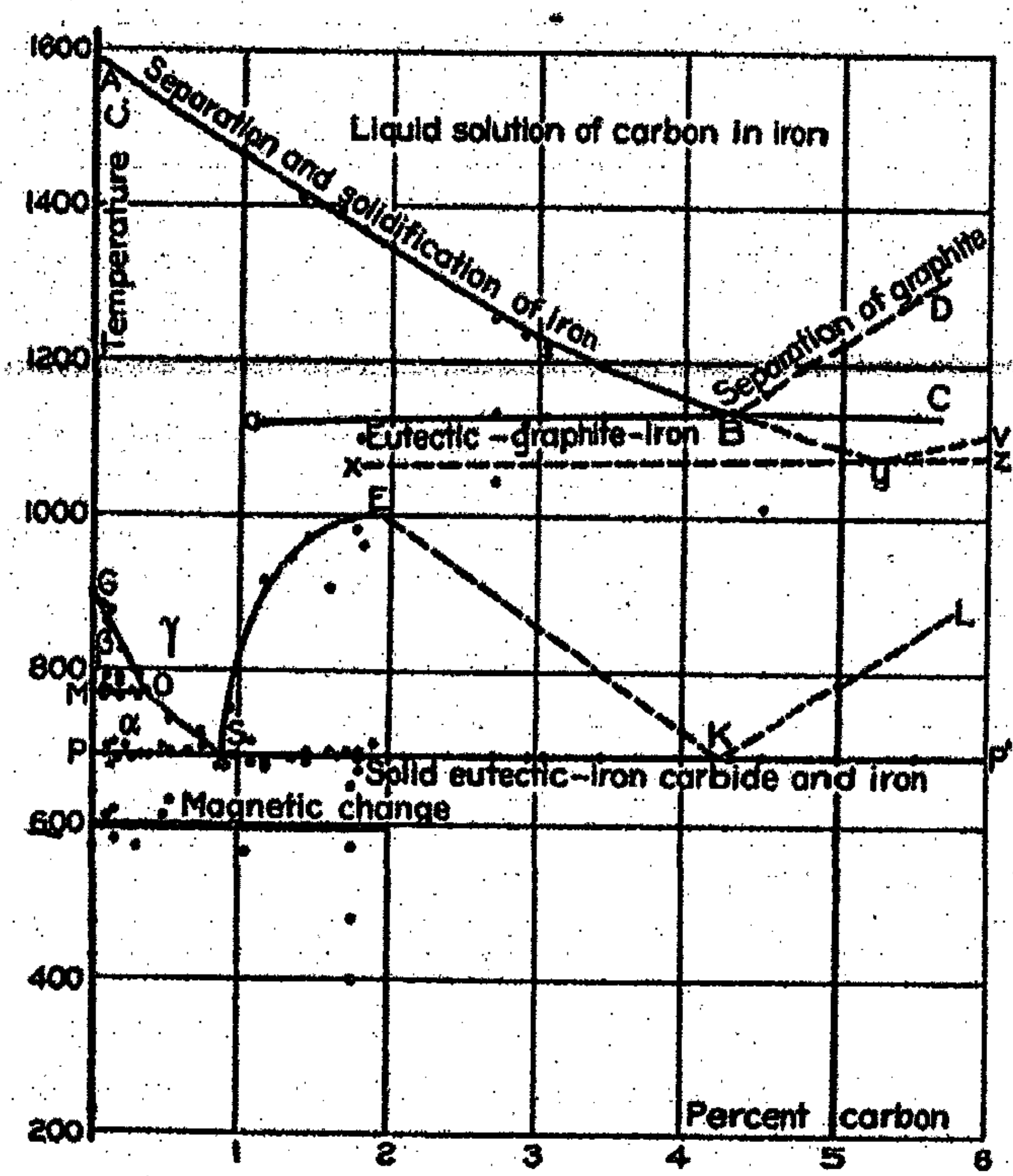

Fig. 1

In discussing any equilibrium diagram it will be worth while to remember certain consequences of the phase rule.

In a system of two components we may have *in equilibrium* at any temperature and concentration at most only two phases, or constituents, of an alloy. The boundary line between two two-phase fields must be either vertical or horizontal, that is, either a line of constant concentration or a line of constant temperature. A vertical between two two-phase fields means a chemical compound. The boundary line between a two-phase and a single phase, or between two single-phase fields, can run in any direction on the equilibrium

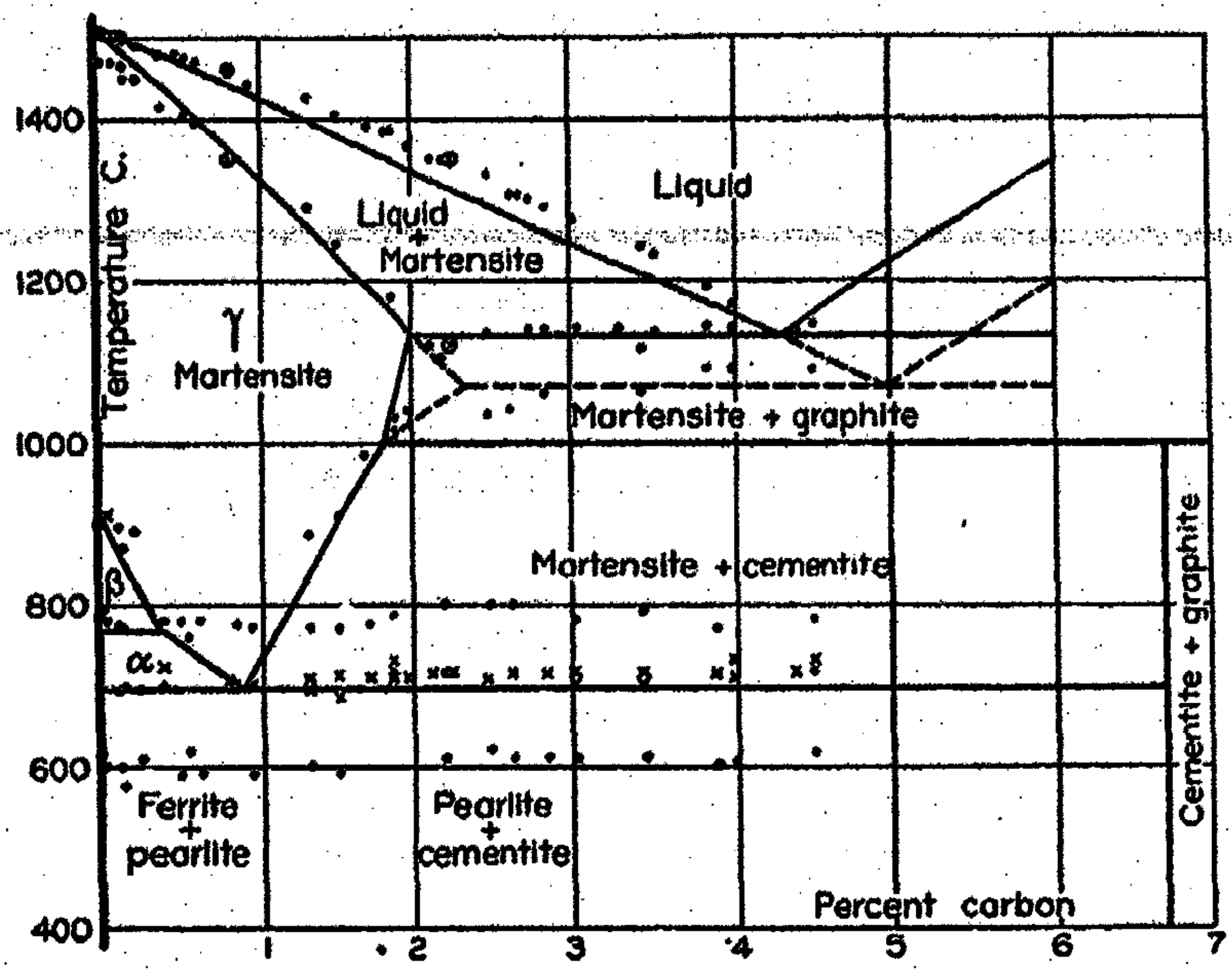

Fig. 2

diagram. Conversely, if the boundary between two fields is proven to be a sloping line and one of the fields known to be two-phase, the other must be single-phase. These and similar things are of course elementary; yet by keeping them in mind work can be facilitated and many absurd mistakes (made even by well-known metallographists) will be avoided.

Through an oversight by Roozeboom two of the fields of his diagram are incorrectly labeled. These are the β and α fields on the zero carbon side of the diagram. In the discussion of the diagram Roozeboom correctly made these $\beta + \gamma$ and $\alpha + \gamma$, as they must be by his assumption of zero solubility of carbon in β and α iron. The fields are by microscopic observation readily shown to be two-phase.[1]

Despite its author's own statement that this diagram was incomplete, it was widely hailed and long accepted as the last word of physical chemistry on the system iron-carbon. Its obvious failure came with the cast irons. An iron may readily be cast white, with all of its 3 or 4 percent of carbon in solution or combination. On annealing at a red heat, say between 800° and 1000° C, this iron will generally, in fact almost always, grow graphite. The diagram calls for an equilibrium state of martensite plus cementite, *without graphite*. The prolonged heating should make the iron approach the equilibrium state. So here was an *impasse*, a flat and inexplicable contradiction.

On this account the validity of the Roozeboom diagram has been vigorously attacked in the last two or three years, notably by the German metallographists. Their present attitude is well summarized in an article by Dr. Carl Benedicks.[2] The figures of this article are reproduced in Fig. 3 and Fig. 4. Heyn first suggested[3] that the stable system was really iron-graphite, and that by somewhat more rapid cooling (supercooling) the system iron-iron carbide might be reached and remain as a metastable equilibrium in the steels and low-carbon alloys. Ruer admits the solubility of carbon in the allotropic form of iron crystallizing from the melt, and draws a line slanting slightly downward from the end of the eutectic to represent the decomposition of the solid solution into α + graphite. Benedicks took an iron with C 3.9 percent, Si 0.75 percent, Mn 0.37 percent, P and S negligible, and heated and cooled it two to five times between

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[1] Heyn: "The Constitution of Iron-carbon Alloys," Iron and Steel Mag., May, 1905, pp. 407 to 417; Zeit. Elektrochemie, 9, 491 (1904).

[2] Metallurgie, 1908, Heft 2.

[3] Zeit. Elektrochemie, 9, 491 (1904); Iron and Steel Mag., May, June and July, 1905.

300° and 800° C. He reports from microscopic examination at the end of this treatment that the material was reduced to ferrite + graphite. Then heating specimens, thus reduced to ferrite + graphite, at 940° C for one or two hours, and quenching, all the usual martensite-sorbite-cementite, etc., structure was found. This he argues to show that some graphite had gone back into solution, and deduces a solubility curve for carbon in solid iron as shown in Fig. 3. In a note appended to the article Benedicks says that Heyn has given up his first diagram and now accepts one intermediate between those of Ruer and Benedicks.

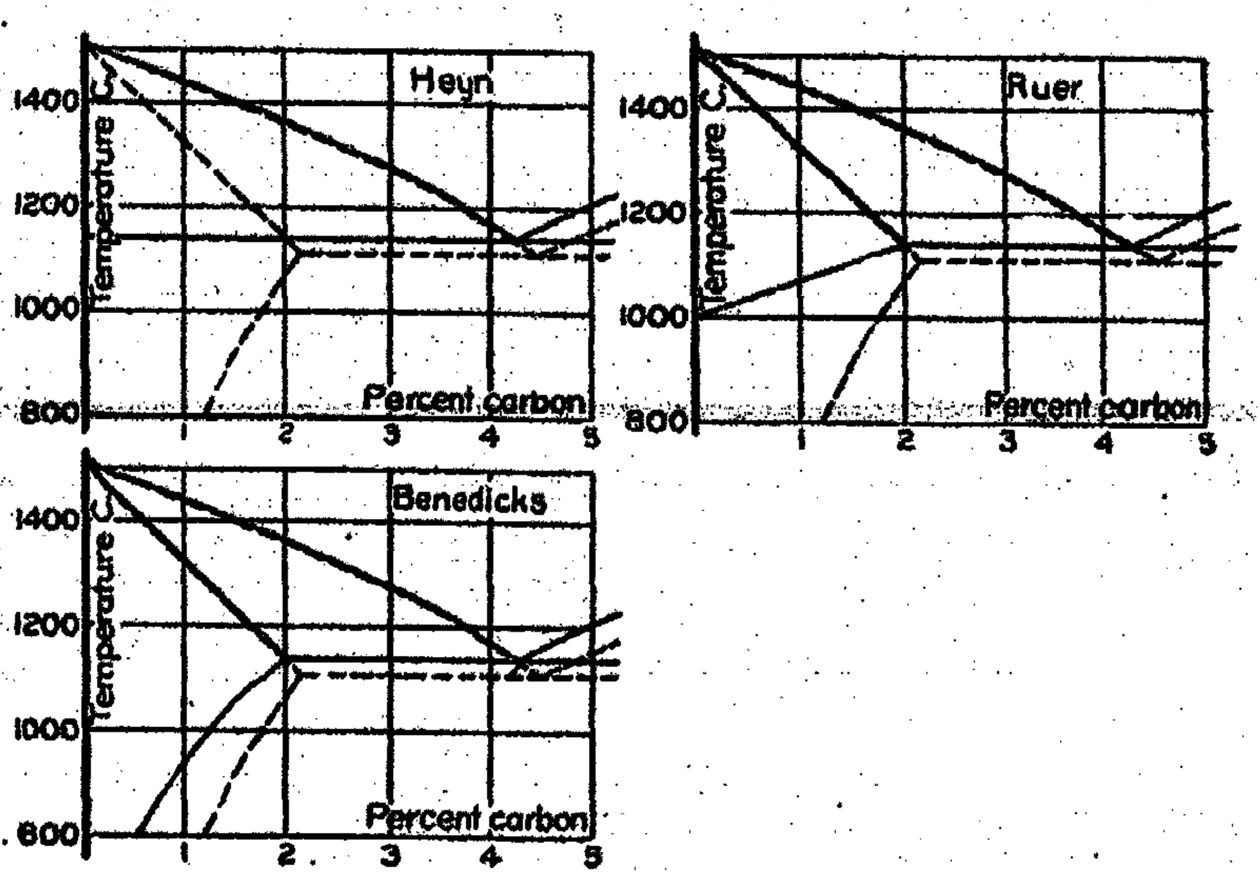

Fig. 3

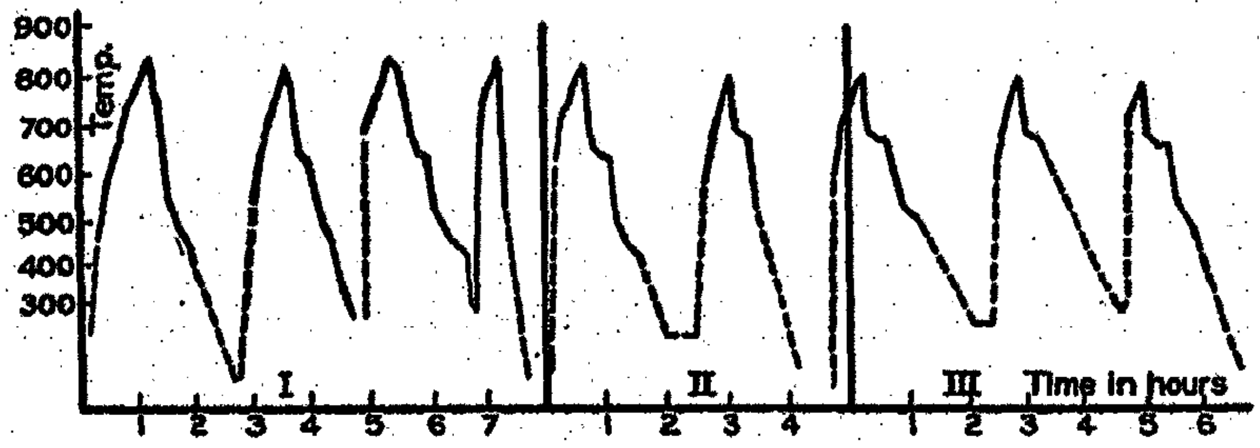

Fig. 4

Some comments on this work and diagram of Benedicks may be pertinent. (1) The silicon present was in solution in the iron. The manganese acts essentially like iron, except that it is able to take care of very slightly larger proportions of the other elements. Correcting for the silicon[1] in solution the carbon solubility line from 800° to the eutectic temperature would displace the solubility line to the right and make it practically coincide with the broken line of the metastable system. That is, Benedicks has proven that the "stable" and "metastable" diagrams are substantially coincident down to 800°. (2) Benedicks gives, in his paper, curves showing the temperature changes of the metal during a treatment of repeated heating and cooling, which supposedly reduced the material to a two-phase equilibrium of ferrite + graphite. These curves are in reality cooling curves of rather rapid cooling and show the inversions in the usual way. The peculiarity is that the γ to carbide inversion at 700° C continually *increases* in strength, whereas if the carbide were unstable and disappearing this inversion should *decrease* and vanish (see Fig. 4). The evidence of these curves is strong that the cementite was not decomposed, and was not unstable.

Granting for the sake of the argument, that Benedicks did obtain the decomposition to a stable system ferrite + graphite, how can he explain the growth of the cementite-made structures when he heated at 940° and quenched? If, as his diagram supposes, cementite is normally unstable and the cementite metastable equilibrium is formed by supercooling a melt, then the formation of cementite is impossible by reheating short of the melt a piece brought to the ferrite + graphite equilibrium. It is impossible because in heating up toward the melt the tendency to the formation of the stable system from the unstable becomes rapidly stronger. Once the carbide of the metastable system has been eliminated from the material, it cannot return without remelting and

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[1] This correction for silicon will be discussed at length later in this paper.

again supercooling. The fact that Benedicks found cementite structures after heating to 940° and quenching shows that cementite must have a place in the stable diagram. The fact that the cementite recurred in these latter (940° heating and quenching) pieces reduces to an absurdity the assumption that the material had been brought to an equilibrium of ferrite + graphite, and confirms the deduction from the cooling curves that the cementite was neither unstable nor decomposed.

The identification by Benedicks and others of the phase with graphite as ferrite is, I believe, questionable. The reason lies in the magnetic properties of cast iron, more particularly the graphitic "soft" cast iron used in electrical machinery. This iron contains about 3 percent of graphite. Being soft and graphitic it is a comparatively slow-cooled iron, and hence approaches the Benedicks-Heyn ferrite—graphite equilibrium, if there be such an equilibrium. Allowing for the difference in specific gravity between the graphite and the iron, 3 percent by weight of graphite would be perhaps 10 percent by volume. The graphite grains being entirely non-magnetic act like 10 percent of minute voids spread throughout the iron. Such voids increase the flux density in the remaining iron, for the same average density per square unit of section, and also somewhat lengthen the magnetic path. Hence a given percentage of voids affects the permeability doubly, decreasing it once through the change in density of flux and once through the change in length of magnetic path. If the iron is ferrite + graphite its permeability should then be of the order of 80 percent of that of the cast steel used in electrical machinery. Such, however, is not the case; the permeability of the cast iron is only 35 to 40 percent of that of the steel. So far as I find recorded, the identification of this "ferrite" has been always by the microscope. In the face of the magnetic properties I believe the microscopic tests insufficient, and that some other iron-carbon phase has been confused with true ferrite. The identity of this other phase will be discussed later.

For the present, one may note on the cooling curves of Fig. 4 that below the carbide inversion point at 700° there is another inversion and heat evolution shown at between 600° and 500°.

In the article in which he first proposed the metastable iron-iron carbide diagram Heyn says:[1] "A proof for the fact that the (liquid eutectic) line really corresponds to a eutectic which is in part composed of graphite has not been given by Roberts-Austen. Such a proof has up to the present time not been given, not even by the recent investigations of Carpenter and Keeling, although the latter investigators without more ado follow the opinion of Roberts-Austen. One is, therefore, justified, till further evidence is advanced, in expressing doubt as to the correctness of this conception. Under the microscope graphite is indeed often enough observed, but never anything which resembles a eutectic of graphite and any other structural constituent." Heyn then discusses the difficulties of the Roozeboom diagram with the cast irons, and proposes the combination of stable and metastable equilibria shown in Fig. 3.

A piece of recent work bearing on the phases separating from the melt is by Goerens and Gutowski.[2] By an ingenious process they quenched and examined the structure of both hyper- and hypoeutectic irons at various stages of the freezing at the eutectic temperature (1140° C). They show that in the hypoeutectic iron (C = 3.75 percent about) the crystals coming from the melt as it crosses the liquidus temperature are "pine-tree"-shaped solid solution crystals of carbon in iron. This is a usual shape for crystals deposited from a solution supersaturated by cooling. Secondly, during the stay at the eutectic temperature come kernels which resolve into graphite ("wurmartig") and solid solution, the latter now of course without the "pine-tree" crystal form. The

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[1] Iron and Steel Mag., July, 1905, p. 42; Zeit. Elektrochemie, 9, 491 (1904).

[2] "Experimentelle Studie über den Erstarrungs und Schmelzvorgang bei Roheisen," Metallurgie, 1908, Heft, 5.

test pieces used were of only 2 or 3 grams weight, quenched in ice water immediately on leaving the furnace. It is interesting to note that under these circumstances the still liquid portion of the pieces did not solidify with retention of the internal structure of the liquid but was partially decomposed. The authors make the unfortunate mistake of calling this background structure of partially decomposed frozen liquid the "eutectic," which it is not. The eutectic is the kernel structure, resolving into graphite and solid solution under the high powers of the microscope. Interesting also and significant are the "cementite" needles which *show from the partial decomposition of the solid solution of the crystals, lying upon and through them.* In the case of the hypereutectic pieces the structure was the same, except that instead of "pine-tree"-shaped crystals of solid solution graphite came from the melt below the liquidus. The kernel structure duplicated. The conclusion at the end of the paper that graphite comes from the decomposition of cementite is peculiar indeed, as no iron-carbon diagram yet proposed calls for cementite at a temperature of 1140°; and their own photomicrographs should have shown the authors that all the "cementite" was itself a decomposition product of the solution crystals, and had nothing to do with graphite.

This work settles the fact that the phases crystallizing in the liquid eutectic are graphite and a solid solution of carbon in iron. The reason that Heyn had never seen a true eutectic structure of these phases is the readiness to inversion of the solution crystals. Without working especially for it, as did Goerens and Gutowski, the eutectic structure will never be seen, but instead something produced from it by later inversions and more or less complete decomposition of one of its phases. The tremendous inversion velocity of the melt, partially decomposing under the ice water quenching of very small test pieces, almost the most rapid quenching available to metallography, most strongly negatives any assumption that this melt can by a cooling only slightly more rapid than that of sand-casting be supercooled to a metastable equilibrium. The large heat evolution and great rapidity of change in the solid solution to cementite inversion at 700° C and the reversibility of this inversion likewise argue that this must be an inversion in a stable, and not a metastable, equilibrium.

I have already noted that Professor Roozeboom himself gave warning that his diagram was incomplete. How much it was so can be judged from Fig. 2, giving the cooling curve data of Carpenter and Keeling,[1] a far more accurate and complete set of determinations of inversion temperatures than that of Roberts-Austen. The apparent temperature rise with increasing carbon in both the liquid and the solid eutectic, which Carpenter and Keeling insisted was real, is explained by variable supercooling, less as the amount of the phase inverting is greater. A constant temperature line at 600°, which was found by Roberts-Austen but not used by Roozeboom, is amply confirmed and is extended across the diagram up to the limit of carbon experimented with, 4.5 percent. Another line at a temperature of about 800° extends across from about 0.8 percent C outward. This line was unknown both to Roberts-Austen and to Roozeboom.

In view of the extremely rapid inversion of the melt shown by the work of Goerens and Gutowski, and the fact that the alloys giving to Carpenter and Keeling their data of inversions were furnace-cooled, the assumption of unstable equilibrium cannot be made against them. The 800° and 600° inversions are weaker heat points than the better known inversions; and at the cooling rates hitherto usual in iron-carbon work (10° C or more per minute) are masked and lost.

In some way the work of Carpenter and Keeling failed of the attention it deserved. During the wide-spread and active discussion of the iron-carbon equilibrium carried on since 1904 by Heyn, Wüst, Benedicks, Howe, Sauveur, and others, practically no notice has been taken of the data of

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[1] Iron and Steel Inst. Jour., May, 1904; Iron and Steel Mag., June, 1904.

Carpenter and Keeling, and no attempt whatever has been made to account for, explain, or utilize their results.

Obviously if Roozeboom had known of the 800° and 600° inversions his diagram would have been far different. Two more inversions mean two more phases. Is it not probable that the identification and description of these phases, the determination of the necessary new fields of the diagram, will clear up the problem of the cast irons and make unnecessary all the machinery of a combination of stable and metastable equilibria?

That such is the case I will attempt to show. Now, heating or cooling curve observations of inversion temperatures give us in the equilibrium diagram only horizontal or slightly inclined lines. Vertical lines in the diagram must be found by other methods, such as microscope observation or, if the phases can be so separated, chemical analyses of a series of alloys of varying concentration and constant heat treatment. Granting the new horizontals (at 600° and 800° C), the lacking lines to complete the Roozeboom diagram are the verticals.

Both Wüst, and Carpenter and Keeling, in carrying out investigations on inversion temperatures, have made up series of practically pure iron-carbon alloys. These alloys were furnace-cooled and should give us some indication of the conditions of equilibrium. In Fig. 5 (from Table IV) I have plotted the analyses of these alloys, none of which contained a total of over 0.15 percent of all other elements than iron and carbon. The ordinates are graphite and the abscissas total carbon. As the reactions between iron and graphite are extremely slow below 700° to 800° C, the graphite to total carbon relation here traced must have originated above 800° C. One peculiarity in the disposition of the points will strike the eye: graphite remains practically at zero up to 3.5 percent carbon, then above that suddenly approximates to total carbon minus 1.4 percent. A vertical line of the diagram, such a line as we are trying to locate, means a chemical compound. Calculation shows that Fe_6C contains 3.46 percent carbon.

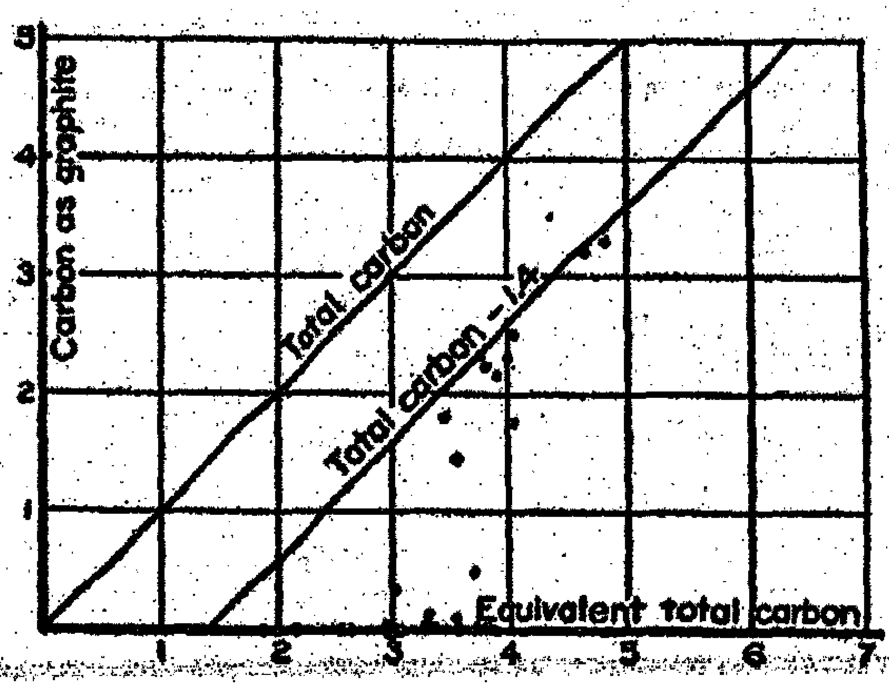

Fig. 5

Observations which made difficulty for the supporters of the Roozeboom diagram were those of Saniter on the decomposition of Fe_3C at high temperatures. On the basis of the original Roozeboom diagram Fe_3C was stable up to 1000° C or thereabout. Saniter found[1] that Fe_3C, heated in nitrogen to 800° to 1000° and slowly cooled, gave out graphite. The data were as follows:

Material analyzed	First sample		Second sample	
	Combined C Percent	Graphite Percent	Combined C Percent	Graphite Percent
Original carbide......	6.73	0.19	6.46	0.22
After heating in nitrogen to 800° and gradually cooling..	5.72	0.40	—	—
After heating in nitrogen to 1000° and gradually cooling..	*3.63*	2.50	*3.79*	2.41

The temperatures are to be regarded as approximate only. The significant analyses I have italicized. Equilib-

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[1] Metallographist, 5, 215 (1902).

rium was approached, but not reached. Comparing the results here with those above from the graphite content of slow-cooled irons, Saniter's work is a remarkable confirmation of the conclusion that between 800° and 1000° there is a carbon-containing phase with a carbon content of practically 3.5 percent.

Assuming the compound Fe_6C the 800° inversion immediately becomes the breakdown of this compound to $\gamma + Fe_3C$ (see Fig. 11). The 800° inversion line would run from near 1.0 percent carbon across the diagram. The assumption of Fe_6C must be justified by showing: (1) that it explains the graphite to total carbon relation in pure iron-carbon, plotted in Fig. 5; (2) that it similarly explains the carbon disposition in commercial cast irons, white or gray. Some such phase as the Fe_6C, a phase occupying a similar position on the diagram, is of course necessary to account for the 800° inversion and the other phenomena discussed above. For the present I leave out of consideration the direct proof by microscopic examination of an iron with 3.5 percent carbon, annealed to equilibrium at 900° to 1000°.

(1) Let any pure cast iron of less than 3.5 percent carbon be slowly cooled from the melt. In passing through the γ + graphite region (Fig. 11), graphite will be thrown out in a finely divided state. The amount of the eutectic being small and the temperature limits of the field narrow, this graphite will have little time to grow. Passing into the $\gamma + Fe_6C$ field the temperatures are still very high, and as graphite is not a stable phase it should disappear, recombining with the iron. Try a similar cooling with the total carbon 4 percent or more. The larger amount of liquid eutectic means a longer halt in the γ + graphite region and the formation there of a much larger quantity of less finely divided graphite than in the previous case. Graphite is now a stable phase down to 800° or even lower, and the larger size of graphite particles makes them very slow to react with the iron. Result, a graphite content in the cold iron approximating that normal to the γ + graphite field. It will be noted in

Fig. 5 that up to 4.0 percent carbon there is still in the furnace-cooled pure irons a considerable recombination of graphite.

It is of course possible to take any iron with over 1.4 percent carbon, hold it artificially at 1100° for some time, then cool rapidly, and so obtain all carbon above 1.4 percent as fairly large-grained graphite.

(2) In considering the commercial cast irons it is evident that some method must be found to determine or compensate for the effects of the elements other than iron and carbon, *viz.*, silicon, manganese, phosphorus, and sulphur. Nearly all the data so far found on the replacing powers of these elements against carbon have to do with the change in the carbon content of the eutectic and are inapplicable to the present problem. Happily, Max Orthey has published[1] the data given in Tables I, II, and III, and plotted as curves in Figs. 6, 7, and 8. In each case the cooling rate of the castings and all of the chemical elements except the one under investigation were kept as constant as possible. The result is therefore a determination of the displacing power of the element against carbon. Drawing in carefully the average straight line curves, the slopes of the lines give the displacing power: silicon, +0.47; manganese, —0.03; phosphorus, +0.03.

Ledebur in "Eisenhüttenkunde" suggests that the displacing powers of silicon, phosphorus, and sulphur are equal to the ratios of the atomic weight of carbon to the atomic weights of the other elements—that is, the replacement is atom for atom. Benedicks has used a similar atomic equivalence in his work on electrical conductivities. That the atomic ratio should be true for silicon, closely related chemically to carbon and forming similar compounds, seems reasonable enough. For phosphorus and sulphur, with their compounds widely different in general from those of carbon, it seems questionable.

In the silicon steels the silicon forms are isomorphous

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[1] Metallurgie, 7, 199 (1907).

with those of carbon; and silicon, having the greater combining heat with iron, will displace carbon in solution or combination. The ratio of atomic weights of carbon and silicon is 12.0 ÷ 28.4 = 0.423; if to this be added a slight correct-

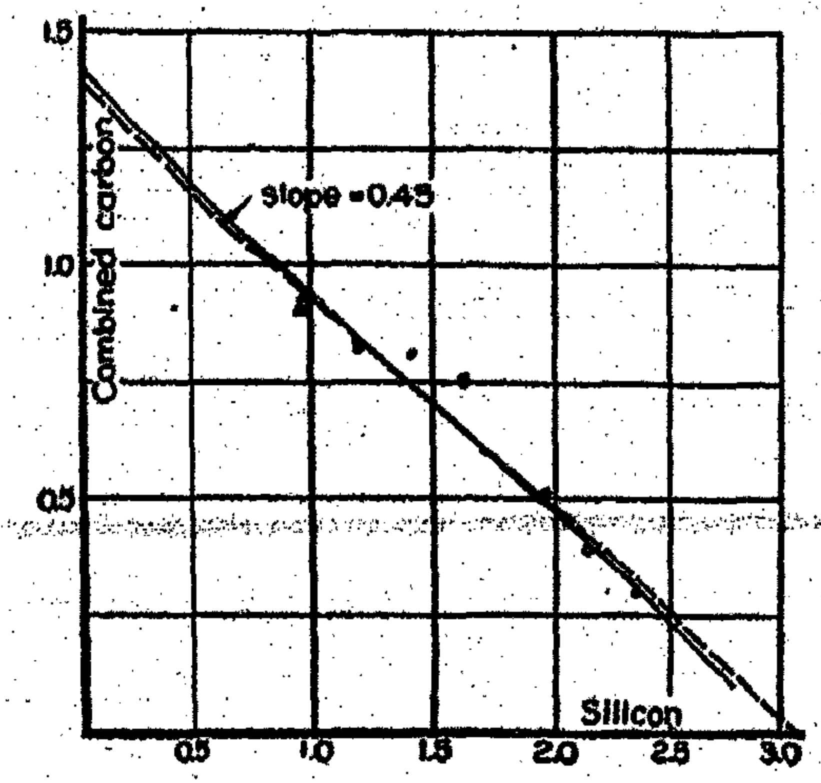

Fig. 6

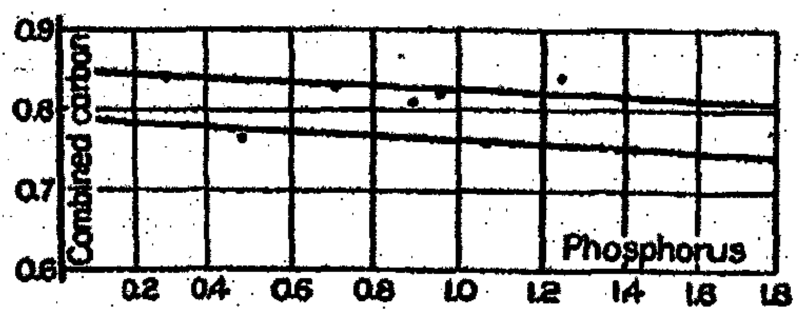

Fig. 7

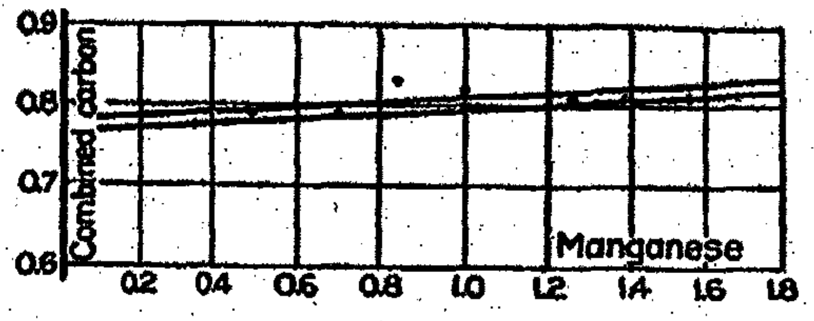

Fig. 8

ive term for the additional iron represented by the difference of weights of the silicon and carbon, the calculated displacing power of silicon is 0.45. This is easily within the limit of experimental error of the number 0.47 determined from

Orthey's data. 0.45 will therefore be used henceforth in this article as the displacing power of silicon.

It seems probable from the usual condition of sulphur and phosphorus in steels and cast irons that carbon will displace them from solution in iron and drive them into the next stage, chemical combination. They would then affect the carbon relation to the iron only as they reduce the amount of iron available to the carbon and thus increase the carbon concentration in the remaining iron. On this basis 1 percent of phosphorus would affect the carbon in cast irons in the same amount as the addition of (approximately) 0.10 percent more carbon; and the sulphur factor would be 0.05.[1]

This value for phosphorus is of the same order of magnitude as the experimental 0.03 from Orthey's data, and within the error of determination. For sulphur no direct determinations of displacing power are available. Such direct computations as I have tried are as often positive as negative, all of small numerical values.

Manganese is in a different class from silicon, phosphorus, and sulphur, as it combines with them just as the iron does, but with somewhat higher percentages of the other elements in the solutions or compounds. Assuming that the manganese-carbon eutectic, with 7.6 percent of carbon, is similar to the iron-carbon eutectic with 4.3 percent, the added carbon-holding power from 1 percent of manganese is (1.6 — 4.3) ÷ 100 = 0.033 percent. This checks as closely as might be expected with the experimental — 0.03 as displacing power from Orthey's data.

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[1] Case 1. Iron and carbon only. C = 4.0 percent; Fe = 96.0 percent. Graphite = about 4.0 — 1.7 = 2.3. (It will be shown later that in the average case, graphite = total carbon —1.7.) Case 2. Iron, carbon and phosphorus. C = 4.0, P = 1.0, Fe = 95.0. In Fe_3P $Fe_2 : P$ = 5.42 : 1. Fe left for C is then 95.0 — 5.42 = 89.58. As compared with the previous case, carbon density in iron is relatively 4.0 × 96.0 ÷ 89.58 = 4.28. Graphite is then 4.28 — 1.7 = 2.58. But the iron-carbon is now only 100 — (5.42 + 1) = 93.58 percent of the total alloy. Hence, relative to the total alloy graphite = 2.58 × 93.58 ÷ 100 = 2.43 percent. That is, roughly, one percent of phosphorus has increased graphite by 0.10 percent. Similarly, one percent of sulphur in FeS would change graphite by 0.05 percent.

If an iron were of such a total carbon content as usually to throw out 3 percent of graphite, adding 1 percent of silicon, which displaces carbon from solution, would increase the graphite to 3.45 percent, all other variables remaining constant. The same result in graphite content would come from adding 0.45 percent to the total carbon (see Fig. 5 and Fig. 11—graphite approximates total carbon minus a constant). In its effect upon the relations of iron and carbon to each other, 1 percent of silicon acts like 0.45 percent of carbon. A "carbon equivalent" of the silicon may then be computed as equal to 0.45 times the silicon; adding this to the total carbon will give an "equivalent total carbon" which will exhibit the same relationships of carbon to iron as the original silicon-containing alloy. This is the meaning and use of the displacing powers of the elements.

As manganese and phosphorus have such low displacing powers, and the opposite signs cause them more or less to compensate for each other, and as the sulphur content of cast irons is generally low and its displacing power small, I have in Tables IV and V found an "equivalent total carbon" corrected only for the silicon. Five percent of manganese or phosphorus, with displacing powers from the curves of Orthey's data ±0.03, would make only 0.15 percent change in equivalent carbon, a change which is for the present negligible. The analyses of commercial irons in these tables are from various sources, as indicated in the tables, and are nearly all of iron in the form of "pig," which is comparatively slow-cooled from the melt.

With ordinates graphite and abscissas "equivalent total carbon," compensated for silicon only, Fig. 9 is plotted just as was Fig. 5 with the pure irons. For purposes of comparison Fig. 5 is included in Fig. 9 in the (+)-shaped points. *The substantial identity of the disposition of the points for chemically pure iron-carbon and for all sorts of cast irons is apparent.* The analyses of cast irons used were taken anywhere and everywhere, without selection of any kind.

The even distribution of the (Δ) points for irons with high manganese justifies the low value for the manganese displacing power. The slight segregation of (o) points for irons with phosphorus over 1.5 percent, along the 45° line representing total carbon minus 1.3 percent may indicate a displacing power for phosphorus as high as 0.10, just as was found above by computation. Even then a correction for phosphorus would scarcely be necessary in ordinary irons.

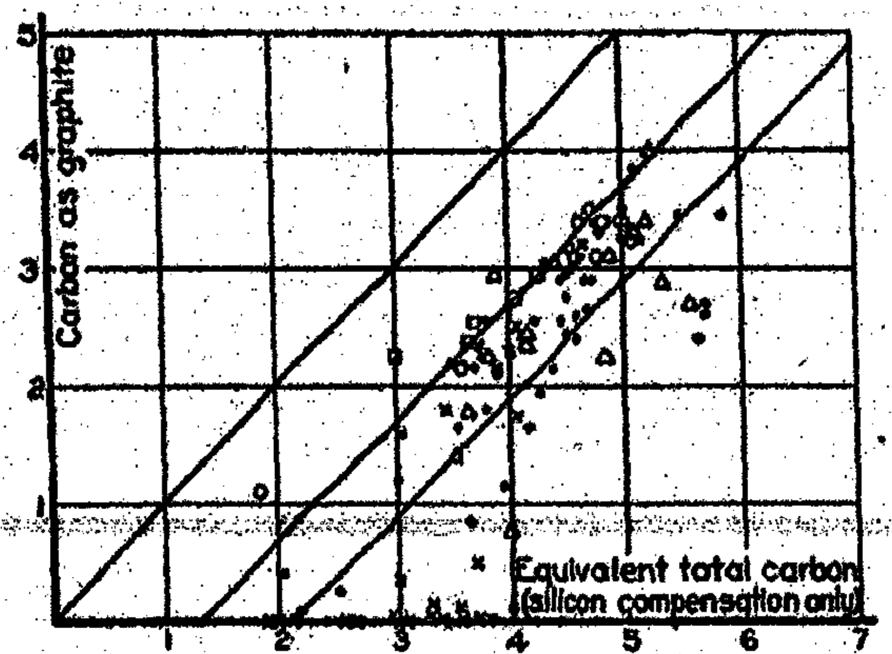

Fig. 9

Fig. 10 repeats Fig. 9 on a slightly enlarged scale of abscissas, and with complete compensation for all of the elements—equivalent total carbon now equal to (total carbon + 0.45 silicon + 0.10 phosphorus + 0.05 sulphur — 0.03 man-

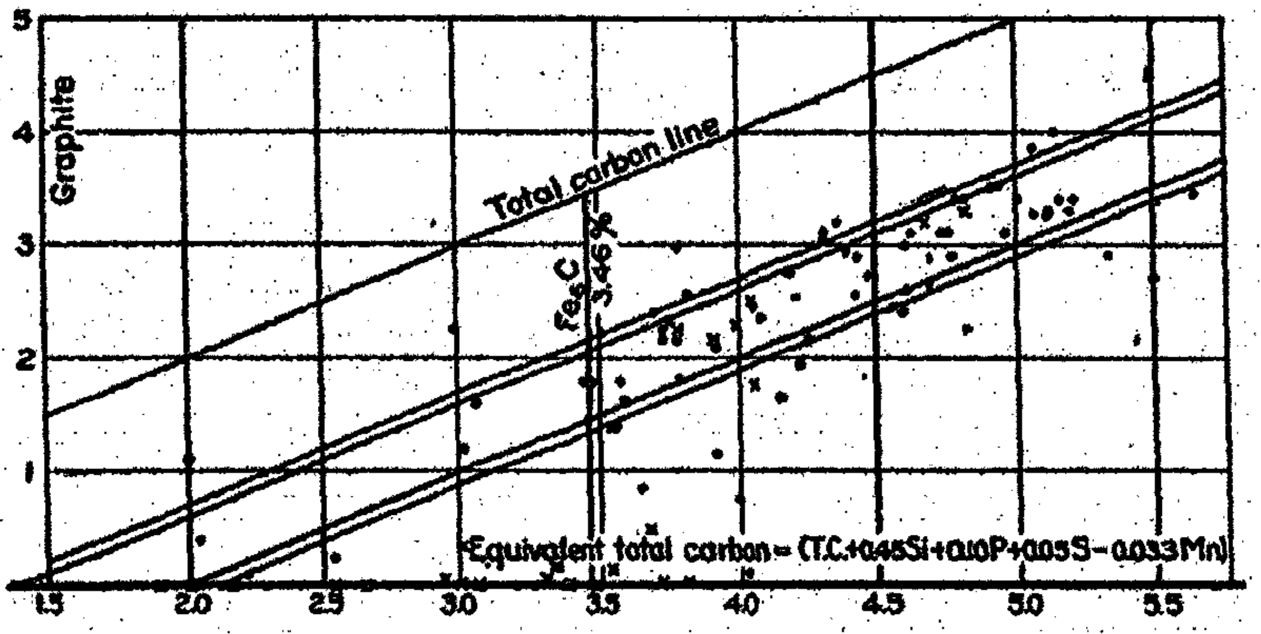

Fig. 10

ganese). It has been mentioned that the analyses are nearly all from pig irons, fairly slow-cooled. Referring to Fig. 11, it will be seen from the γ + graphite field that the graphite content of such a fairly slow-cooled iron should lie between the limits indicated by the points B and C. Recombination of graphite in the γ + Fe_6C field, or Fe_6C + graphite field, may of course reduce the graphite below that shown

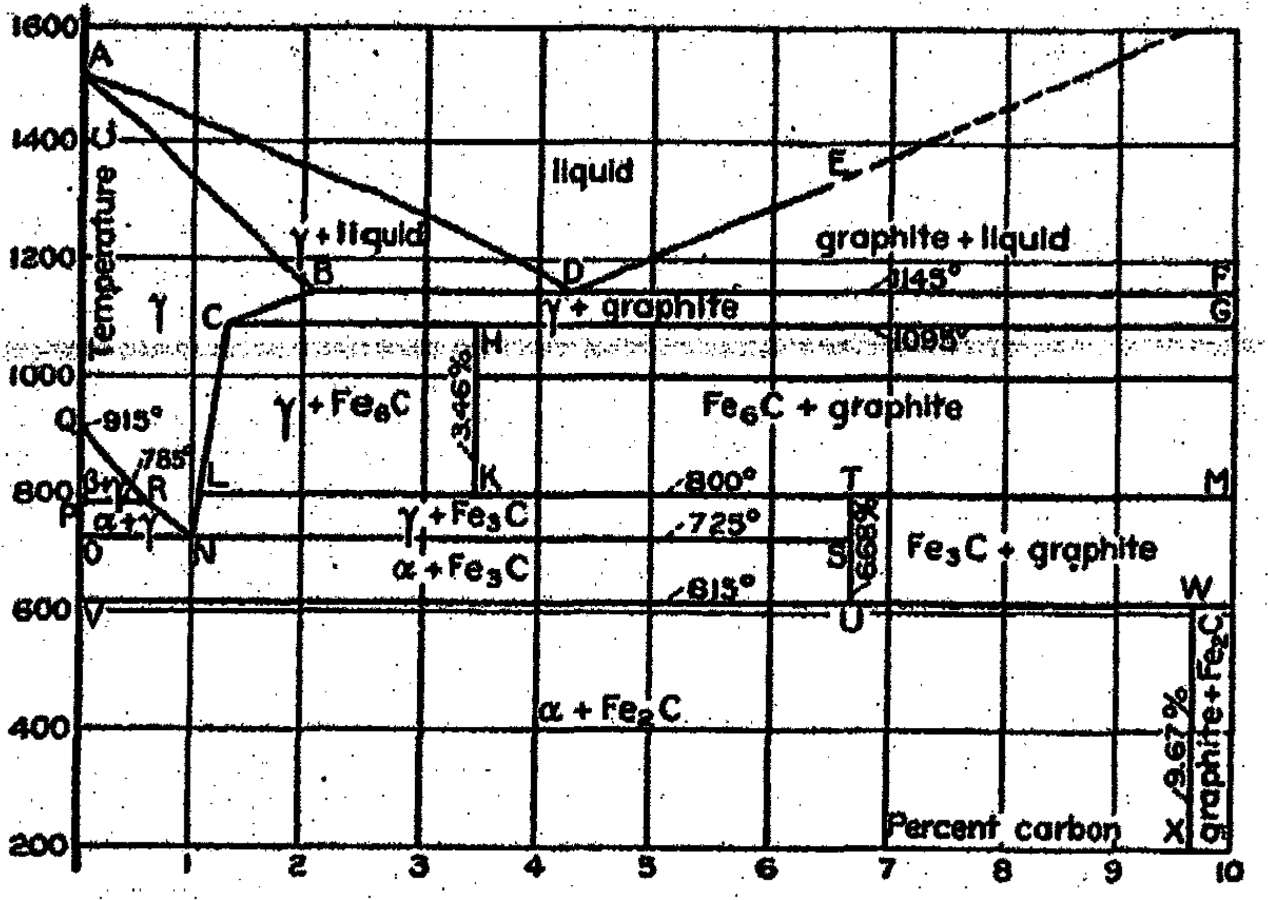

Fig. 11

at B, in the eutectic. The two sets of double lines in Fig. 10, parallel to the total carbon line, and at constant distances below it, serve to locate the carbon concentrations for the points B and C of Fig. 11. B would come at from 2 percent to 2.1 percent carbon, C at 1.3 to 1.4. The location of B at 2.0–2.1 percent is identical with that from the cooling curve work of Carpenter and Keeling.

We have now reached a position where we can consider the last variable affecting the carbon disposition, namely, the cooling rate of the castings. The work of Goerens and Gutowski, cited above, proves the very great rapidity of inversion of the melt, so great that it is impossible to freeze the melt to any other than the normal γ + graphite inversion. This great rapidity of inversion makes it fairly certain that in sand casting all irons will in freezing throw out from the melt at least the graphite corresponding to B in Fig. 11. In "chill" casting some of the carbon will be held in solution in the partially decomposed frozen liquid, and the effect is to throw the point B (Fig. 11) out to the right. The average compositions of the various gray and white irons are as follows:[1]

Kind of iron	Silicon	Total carbon	Graphite	Equivalent total carbon
Ordinary gray	2%	3.5	3	4.50
Light gray	1 to 1.5	3.0 to 3.5	2+	3.85
Half white	1	2.5 to 3	Small	3.75
White	0.8 or less	3.0 or less	None	3.4 or less

Comparing the graphite and equivalent total carbon here shown with Fig. 10 we see: (1) the graphite agrees well with Fig. 10; (2) the white and half-white irons come within, or under, the influence of the phase Fe_6C. By the presence of the "chill" in the mold, the point B (Fig. 11) is thrown sufficiently to the right to keep all the carbon in solution. This supersaturated solution, of course, partially inverts at lower temperatures. The extreme hardness of chilled cast iron is due to the presence of this partially decomposed solid solution. It is interesting to note that equilibrium or even very slow cooling will give in these white irons, from the recombination of graphite in the γ + Fe_6C field, the same negligible graphite content as the chilling. The other phases and the physical properties, however, would be very different. With higher equivalent total carbon than 3.75, the heat change at the eutectic is so large that no ordinary "chill" can prevent the throwing out of some graphite. The rapidity of cooling can then operate only to hold the graphite practically to that normal at the line of the eutectic

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[1] Compiled from various standard metallurgies, mostly Ledebur.

temperature, and prevent the breakdown of γ to γ + graphite along the line BC, Fig. 11.

The average graphite content of iron-carbon with varying equivalent total carbon can be stated as follows: Up to 3.5 percent, graphite is zero or nearly so; from 3.5 percent to 4.0 percent, graphite depends on the cooling rate, varying all the way from 0 percent to 2 percent; with equivalent carbon greater than 4.0 percent, graphite averages 1.7 percent less than the equivalent total carbon. The maximum graphite possible in any case is equivalent total carbon minus 1.3 percent (point C, Fig. 11). With over 4.0 percent equivalent carbon, rapidity of cooling may vary the graphite 0.4 percent either side of the average, slow-cooling increasing, and rapid-cooling decreasing, the graphite.

One phenomenon with the white irons has been one of the main troubles with the Roozeboom diagram, and has lent great strength to the supposition of a combination of stable and metastable equilibria existing simultaneously, with the stable system iron-graphite. This phenomenon is the occurrence of temper-carbon, called also temper-graphite, or annealing carbon. An accompanying phenomenon is the so-called "decomposition of the carbide."

Of these phenomena I will now attempt a description and an explanation. When a chill-cast or moderately quickly cooled "white" iron is heated to a red heat, there are usually observed in it small nodules of a brownish or brownish black extremely finely divided, perhaps amorphous, graphite. This is called temper-carbon from the heat treatment used in its formation. The apparent structure of the white iron before heating is expressed as cementite + pearlite. Simultaneously with the appearance of the temper-carbon the cementite + pearlite structure seems to decompose. Referring to Fig. 11, and remembering the rapid cooling of these irons from the melt, their expected constitution is not cementite + pearlite, but a supersaturated solid solution in various stages of beginning decomposition. The melt is not instantaneously frozen; neither has time been given for the normal decomposition into γ + graphite.[1] I need not explain that a partially decomposed solid solution would have under the microscope, the appearance of a fine eutectic. As some nearly normal γ crystals must have begun to come from the melt in the first stages of its freezing, the "white" iron would not be homogeneous, but some parts would be more supersaturated than others. Thus the partial decomposition will not be uniform all over a microsection; the appearance under the microscope will be a mixture very well simulating the recognized structure of cementite + pearlite.

On heating up this white iron toward a red heat, this supersaturated solid solution will go through, so soon as increase of temperature gives a sufficiently rapid reaction rate, the same inversion which would normally have occurred during freezing of the melt, but which was then suppressed because of the rapidity of the cooling. An observer watching this reaction would see the solid solution breaking down in minute subdivision; *this is the apparent "decomposition of the cementite."* Simultaneously, from slight migration in the iron, appear the nodules of graphite. This graphite, formed from the decomposition of the supersaturated solid solution, will be extremely fine as compared with the graphite formed in the slow freezing of the liquid eutectic. It is, however, nowise different in kind, but it is a product of the same reaction, with the physical conditions of the reaction differently controlled.

It has been found also that the throwing out of temper-carbon is accelerated by the presence in the iron of a little of previous graphite. This contact influence of previous graphite is readily understood as a parallel case to the adding to a freezing liquid of nuclei of the phases to be formed from it, a practice frequently used to facilitate crystallization.

Without the presence of previous graphite, that is, in a "white" iron with zero graphite, the decomposition of the

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[1] See previous remarks on the work of Goerens and Gutowski, and on the probability of the confusion in identification of these now suggested with the hitherto recognized phases and structures in iron-carbon.

supersaturated solid solution seems not to be rapid until the temperature reaches about 800° C. On continued heating the temper-carbon formed will be reabsorbed unless the composition is such (equivalent total carbon greater than 3.5 percent) that some of the graphite persists as a stable phase, above 800°. In the presence of previous graphite, the formation of temper-carbon begins and goes on at as low a temperature as 700° C.[1]

The reaction rates between iron and temper-carbon, and between iron and graphite, will be different from two causes. First and most important is the difference in size of particles; the temper-carbon is very much more finely divided than the graphite. Secondly, the temper-carbon is usually an unstable phase, and the graphite at least a more stable one. Both of these causes will make for a more rapid reaction between iron and temper-carbon than between iron and graphite.

In nearly all experiments hitherto reported on temper-carbon, the time of heating at high temperatures has been just long enough to throw out the temper-carbon, but not long enough to bring about the equilibrium between iron and carbon. The heating also has usually been in air, which rapidly oxidizes carbon from the outer layers of the specimen. This oxidation, causing a variable and practically unknown concentration of carbon at different parts of the section, entirely nullifies the value of the results.

The results of Charpy and Grenet[2] come under the above criticism. Even though they packed their specimens in charcoal, oxidation of the specimens occurred and the total carbon in the annealed specimens was less, sometimes much less, than the original carbon content. The oxidation takes out solution carbon much faster than it does graphite, and hence gives abnormal values of graphite with reference to

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[1] This was shown by Goerens and Gutowski, and by Charpy and Grenet, whose work is to be discussed shortly.

[2] Bulletin de la Société d'Encouragement, March, 1902. Translated, American Manufacturer, June 5, 1902; and Metallographist, 1902, p. 202.

the average total carbon left in the specimens. The irons used by Charpy and Grenet also contained in some cases large amounts of silicon—up to 2.10 percent. I would not then try to do anything with their data were it not for the fact that their results were the first and principal basis for the supposition of the "iron-graphite" equilibrium system. As solution carbon oxidizes more rapidly than graphite, the only fair reference value for the graphite content is the original total carbon content. Using this, and finding the equivalent total carbon compensated for silicon, etc., I have plotted in Fig. 12 the data of Charpy and Grenet on the same scale as the general data of Fig. 10. The original irons of Charpy and Grenet were white irons, cooled in casting with cold water. The graphite content was obtained by reheating, for various times and at various temperatures. The agreement of Fig. 12 with Fig. 10 is such that it requires no comment. No supposition of a system iron-graphite is needed to explain these results. I might even point out that the decided grouping of their points on the line of equivalent total carbon minus 2.0 to 2.1 gives a good means of locating the normal graphite thrown out from the melt in the liquid eutectic, a determination in complete accordance with that from all cast irons from Fig. 10 and with the cooling curve work of Carpenter and Keeling.

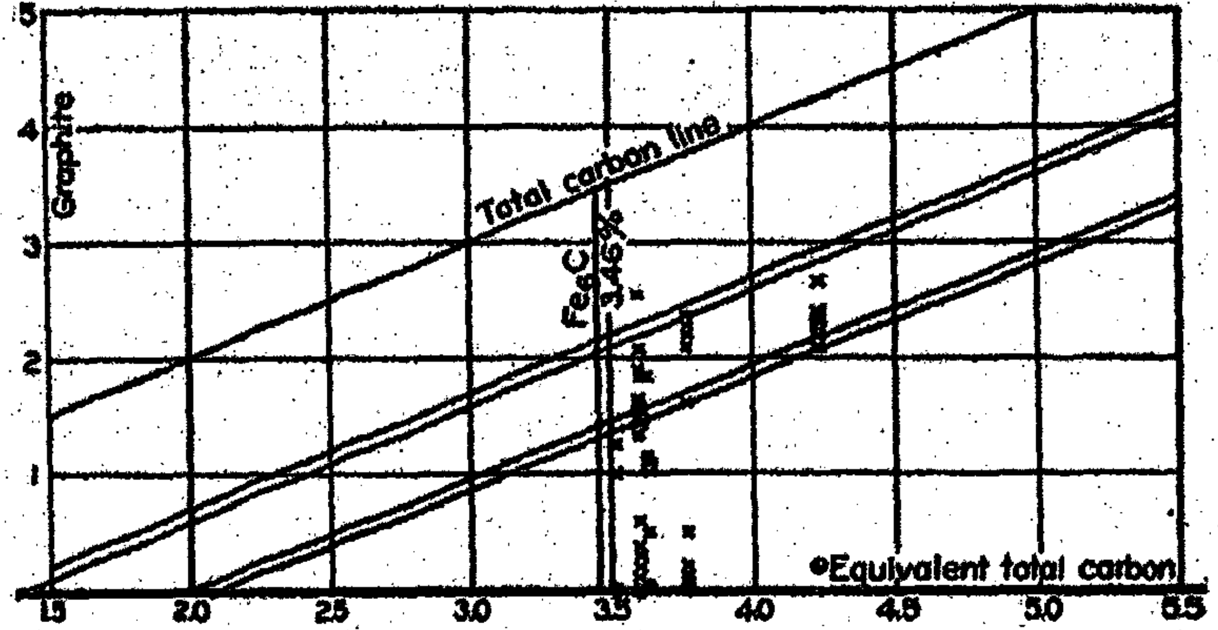

Fig. 12

I have made above, a statement, which may be questioned, that solution carbon is oxidized more rapidly than graphite. In justification I shall discuss a recent article by Wüst,[1] a study of the phenomena of the process of making malleable iron. Wüst refers first to Ledebur's explanation of malleableizing, namely, oxidation at the surface of the iron and migration of carbon from the center to the surface, in an attempt to maintain homogeneity of carbon content. Wüst points out that such migration is possible only for solution carbon, not for graphite, and that the oxidation follows the throwing out of the temper-carbon. For his experiments, Wüst made up a white iron (chill cast in cast-iron molds) of the composition:

Total carbon	4.17 percent	
Graphite	Traces	
Silicon	1.01	(Equivalent total carbon 4.62 percent)
Manganese	0.18	
Phosphorus	0.020	
Sulphur	0.010	

Two hours' heating of this iron in a vacuum at 950° brought out 3.45 percent of temper-carbon (graphite), total carbon remaining unchanged. For malleableizing, specimens of this iron, some white as cast and others with the temper-carbon thrown out, were put into an evacuated furnace together with a charge of iron oxide. The iron and the oxide were sometimes in contact, sometimes not. The temperatures used were from 900° to 1000°; the times of heating from 20 to 110 hours. The total carbon in the pieces was decreased (oxidized out) at a rate of about 0.04 percent per hour of heating, *independently of the previous history of the iron specimens or of its contact with the oxide.* The loss of total carbon was in all cases *where the temper-carbon had been previously thrown out* paralleled by the loss of temper-carbon. From this equality of the loss of total carbon and of temper-carbon, Wüst deduced that the oxidation was directly upon the temper-carbon, and made up a series of chemical reactions

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[1] Ueber die Theorie des Glühfrischens, in Metallurgie, 1, 7 (1908).

to suit his deduction. Rather astounding among these reactions is $3Fe + 2CO = Fe_3C + CO_2$, when Wüst had only a page before explained that the temper-carbon was formed by the reaction, at the same temperature, $Fe_3C \rightarrow$ ferrite + temper-carbon.[1]

The consideration which spoils Wüst's deduction is that the equality of loss of total carbon and of temper-carbon does not hold for those pieces in which temper-carbon had not been thrown out previously to the malleableizing, nor for the different parts of the cross-section of his test pieces. To show this it is necessary to reproduce, with some rearrangement, the tables of Wust's article.

Carbon Analyses

No. of test	Hours of heating	Temperature	Before heating		After heating		Losses	
			Total carbon	Temper-carbon	Total carbon	Temper-carbon	Total carbon	Temper-carbon
I	20	900	4.17	3.45	3.46	2.76	0.71	0.69
II	20	920	4.17	3.45	3.43	2.74	0.74	0.71
III	24	940	4.17	3.45	3.28	2.58	0.91	0.87
IV	26	960	4.17	3.45	3.01	2.29	1.16	1.16
V	26	960	4.17	3.45	1.84	1.10	2.33	2.35
		(1000)						
VI	21	940	4.17	0.00	3.21	2.73	0.96	—(0.72)
		(1000)						
VII	24	960	4.17	0.00	2.98	2.52	1.19	—(0.93)
VIII	20	960	4.17	0.00	3.46	2.49	0.71	—(0.96)
IX	44	960	4.17	0.00	3.12	2.52	1.05	—(0.93)
X	110	940	4.17	0.00	2.52	2.02	1.65	—(1.43)
XI	50	—	4.17	3.45	2.59	1.90	1.58	1.55
XII	52	—	4.17	3.45	2.29	1.52	1.88	1.93

Assuming, as is justifiable, that pieces VI to X threw out in the first hours of their heating the same 3.45 percent of

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[1] I should note that the reaction $3\,Fe + 2\,Co = Fe_3C + CO_2$ has long been the stock reaction to explain cementation and case-hardening of iron by carbon monoxide; and this in face of Saniter's proof, cited above, that Fe_3C is unstable above 800° C, and that the carbon input limit in cementation is around 1.0 to 1.3 percent, instead of the 6.67 percent which expresses the composition of Fe_3C.

temper-carbon as pieces I to V in their preparation, the values in parantheses in the last column can be supplied. It is then obvious that the equality of loss of total carbon and of temper-carbon fails; the loss of total carbon is greater. This is more clearly shown by the analyses from different portions of the same test pieces:

Carbon Analyses

No. of test	Before heating		After heating, average of section		After heating			
					Edge of piece		Center of piece	
	Total carbon	Temper-carbon	Total carbon	Temper-carbon	Total carbon	Temper-carbon	Total carbon	Temper-carbon
X	4.17	0.00	2.52	2.02	1.07	0.21	3.98	3.86
VII	4.17	0.00	2.98	2.52	2.02	1.54	3.97	3.50

Remembering that total carbon was about 0.75 percent greater than temper-carbon, it will be seen that the loss in total carbon outruns that of temper-carbon, and that this difference is greater in the center of the piece. It is most unfortunate that Wüst did not determine the change in silicon content as well as that of carbon; lack of knowledge of what happens to the silicon makes all conclusions from these experiments more or less guesswork. Taken all in all, I should say that the carbon decrease in malleableizing goes on as follows: (1) Near the surface, both solution carbon and temper-carbon are oxidized, the solution carbon more rapidly than the temper-carbon. (2) The carbon decrease in the surface is followed by a diffusion of solution carbon from the center, leaving the temper-carbon there abnormally high. These two actions working together will explain the malleable irons better than the old hypothesis of Ledebur or the more recent one of Wüst.

One other action of iron and carbon at high temperatures remains for consideration—the phenomenon of cementation or case-hardening. The curve of *ready* solubility of carbon in iron should be approximately the line ONLCH in Fig. 11.

This is confirmed by the cementation observations of Mannesmann, Royston, and Saniter. The main observations, those of Mannesmann, have been "doctored" into a smooth curve and are quantitatively valueless; but the general agreement is quite satisfactory. Cementation or case-hardening does not take place below 700°, is slight at 800°, fairly rapid at 900° and quite rapid at 1000°. The limit of carbon input agrees well with the line ONLCH. The carbon goes into the iron, not as usually explained in the form of Fe_3C, but as solution in the γ iron. The Fe_3C results from later breakdown of the γ, as the iron cools at the end of the process.

It is now time to leave off discussion of the 800° inversion, the phase causing it (Fe_6C), and the consequences in the cast irons of the occurrence of that phase, and to take up the 600° inversion and its meaning.

This inversion was found by Roberts-Austen and by him called a magnetic change. That he was mistaken in this is shown by the work of Curie on the magnetic properties of iron. The magnetic change comes with the disappearance of the α allotropic form of iron. Roozeboom knew of this inversion but did not attempt to use it in his diagram. Carpenter and Keeling found the 600° inversion in all the irons they experimented with, from zero up to 4.5 percent carbon, the limit of their concentration. No one, so far as I can find, has offered any explanation or meaning for this inversion.

Many facts can be marshaled to show the activity and importance of this neglected change. First, the well known and feared embrittling of iron and steel by working at a "blue heat." This is working the metal at a temperature of 500° to 550° C, just when the rate of change of phases from the 600° inversion would be a maximum. No other cause for this embrittling of the metal in working at a blue heat has been given, nor, I believe, can be given, than that at that temperature the working promotes some change of phase in the metal, the phase formed being a brittle one. Under the accepted hypothesis that the $\alpha + Fe_3C$ formed by the 700° inversion is normal from 700° downward, no explanation of this phenomenon is possible.

Second, the brittle and "crystalline" fracture of steels submitted for some time to vibratory stressing, or rapidly alternating stressing. The original structure of these steels is strong, tough, and stands up well under fatigue tests. They will not show a crystalline fracture when new. Now, vibratory stressing acts like temperature rise in increasing molecular freedom, and the "crystallization" under vibration loading becomes identical with the "crystallization" from working at a blue heat.

In this connection the recent work of Strohmeyer on the aging of steels becomes of interest.[1]

Strohmeyer made tests on a large number of both good and bad steels to determine if any aging effect could be detected. The test he selected was one of bending of strips, and the particular quantity measured the elongation in the outer fiber of the bent strip. Samples were put for 17 weeks in (*a*) the steam space of a boiler, (*b*) storage at room temperature, (*c*) cold storage at — 16° F (—9° C). The result: "it is found that the frozen samples have preserved 30 percent more elongation than the stored ones, and 50 percent more than the boiled ones—the measure of respective elongation being 24 (original), 12 (stored), 8 (boiled), and 16 (frozen)." Here again is evidence of an inversion going on, even at ordinary temperatures, and going on more rapidly as temperature is raised. To explain this change requires an inversion in the diagram at some temperature below 700° and yet considerably higher than the temperature of the steam space of a boiler.

The phase produced by this inversion has the undesirable physical property that it cannot absorb any large amount of "working" without failure. Until a considerable amount of this phase has been produced in a steel it will

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[1] Jour. of the Iron and Steel Inst., i, 200 (1907), and London Engineering, 432, 642, 725, 757 (1907).

remain tough, and capable of a large amount of shock or vibration stressing. When this new phase has been produced in sufficient quantity it fails under the shock or vibration stressing, the stressing, of course, concentrating its effects on the weakest constituent of the metal, and the result is a fracture through the crystals of the brittle phase. Under slow loading, where the work absorbed has time to distribute through the piece, the strength and ductility may be found satisfactory; under rapid loading or repeated loading the piece will fail from the concentration of stress and deformation on the brittle constituent.

Strohmeyer has proved that the change to the brittle phase goes on at a very measurable rate even at temperatures below freezing. With this cause added to the known stiffening of steels at low temperatures, the failure of rails under the blow of the unbalanced locomotive driving wheels may be more readily explained.

The beneficial effects of certain alloying metals in steels, notably vanadium, would be explained from their depression or suppression of the 600° inversion. Vanadium steels stand up much longer and better under shock than ordinary steels.

A bit of purely metallographic evidence of an inversion below that of 700° C is shown in Fig. 13. This is Heyn's diagram of the relation between percentage area in pearlite and percent of carbon.[1] From zero to 0.5 percent C there is practically 10 percent of pearlite to 0.1 percent C. Then the ratio changes and the curve obtained is OAB, instead of OAC as would be expected. Benedicks found the line AB, without checking for OA, and extrapolating BA downwards deduced that the solubility of carbon in α iron was not zero, but about 0.25 percent. If he had measured the pearlite area in a steel of 0.25 percent carbon he would have found his extrapolation unjustified, as instead of a homogeneous field of solution of carbon in iron practically one-fourth of the field is pearlite.

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[1] Iron and Steel Mag., May, 1905.

Heyn's diagram shows that below the 700° inversion which formed the pearlite there is another inversion which practically does not occur up to 0.5 percent carbon, but beyond that comes in to modify and apparently increase the pearlite area. The tendency to any inversion depends on the amount of the phase inverting, and this new inversion does not occur in significant amount until the carbon content is up to 0.5 percent. It is then an inversion in the carbon containing part of the constituents formed by the 700° inversion; that is, the 600° inversion is a breakdown of the cementite. From the fact that the cementite breakdown increases the pearlite areas, it follows that the phase formed by the cementite breakdown closely resembles the cementite and contains a higher percentage of carbon than does the cementite itself.

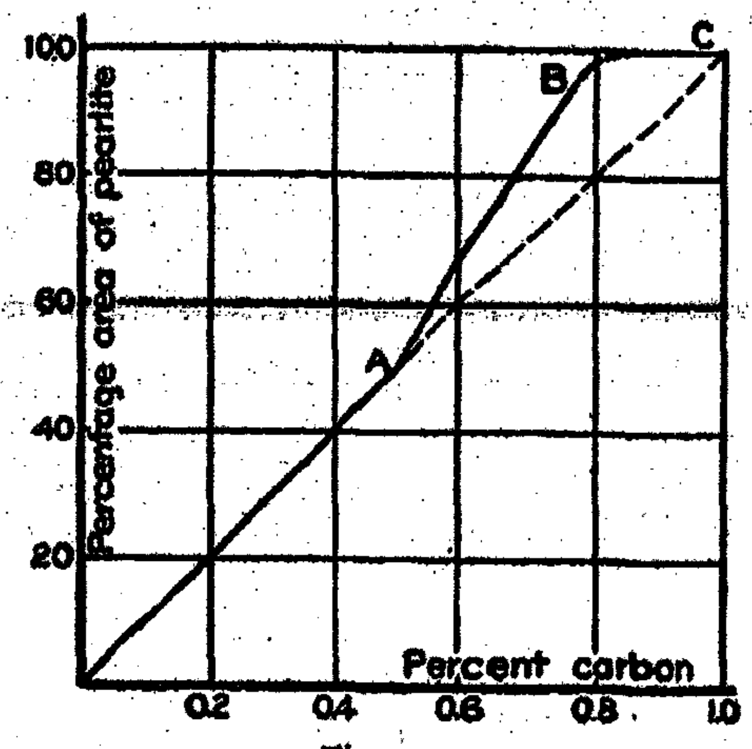

Fig. 13

The line OA, Fig. 13, shows the relation between percentage carbon and percentage pearlite area when unmodified by the 600° inversion of the cementite. Extrapolating this to C, at 100 percent pearlite, would give the true position of the solid eutectic, where γ solution breaks down to α + cementite, as practically 1.0 percent carbon, instead of the accepted 0.85 percent from the curve OAB. B is out of position from the modifying effect of the 600° cementite inversion upon pearlite area; C is the true position (see Fig. 11, point N).

Evidence by chemical analysis of this cementite change, and of the identity of the phase formed by it, was given as long ago as 1902, by Campbell and Kennedy.[1] Previous work by Abel and Deering, Mueller, Osmond and Werth, Arnold and Read, had settled conclusively that the carbide in slow-cooled steels was mostly Fe_3C. Campbell and Kennedy questioned whether the carbide coming out in the presence of a carbon content much higher than that of the steels might not have a different formula. To decide the question they took a white charcoal iron, of combined carbon 3.53 percent, graphite 0.01 percent, silicon 0.07 percent, phosphorus 0.13 percent, sulphur 0.01 percent, and manganese 0.05 percent. This iron in a 900-gram specimen was annealed in an assay furnace in an atmosphere of hydrogen. The heating was such that it took five hours to reach 950° C; the temperature was maintained two hours at 930°–950° C, and then allowed to fall at such a rate that it took about three hours to reach 600°. By reference to Fig. 11, and consideration of the effect of temperature rise on the velocity of chemical reaction and of approach to equilibrium, it is seen that this heating and cooling was practically the ideal one to develop Fe_6C, if such a phase occurs.

Incidentally it may be remarked that the final graphite content was found to be 0.12 percent. As the "equivalent total carbon" is 3.59 percent and 3.59–3.46 (carbon in Fe_6C = 3.46 percent) is 0.13 percent graphite expected by Fig. 11 for equilibrium at 950°, this is a very pretty confirmation of the Fe_6C phase, and of the diagram in Fig. 11.

The annealed specimen was made anode in electrolytic solution in fourth-normal H_2SO_4. The carbides recovered were analyzed and contained from 6.5 up to 9.45 percent

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[1] "The Probable Existence of a New Carbide of Iron," Jour. of the Iron and Steel Inst., 1902, ii; Metallographist, April, 1903, p. 139.

of carbon; the average was 8.20 percent. Separating the carbides, by means of a 200-mesh sieve (40,000 holes per sq. in.) into coarse and fine particles, gave an average of 7.74 percent carbon in the coarse-grained carbide and 9.33 percent in the fine-grained. This last fact is very significant when one considers that Fe_2C, if present, must be there as the product of decomposition of the Fe_3C and therefore much finer-grained on the average than the Fe_3C. Fe_2C would contain 9.67 percent carbon; Fe_3C contains 6.67 percent. Granting the 600° inversion as shown by the cooling curves, the slow-cooled iron would be expected to be a mixture of the phase normal above 600° and that below, the slow cooling not bringing about complete decomposition of the phase normal to the higher temperature. To get equilibrium in iron-carbon alloys at any temperature as low as 600° or below, requires holding a very long time at that temperature.

The above considerations, in conjunction with the uncontroverted work of Carpenter and Keeling on the inversions, from cooling curve data, and of Campbell and Kennedy on the analysis of the carbides from a high-carbon alloy with iron, make it certain that Fe_2C does occur in the iron-carbon equilibrium, and that the 600° inversion is that of decomposition of Fe_3C into Fe_2C.

The iron-carbon equilibrium diagram, as given in Fig. 11, is now explained. It is the Roozeboom diagram, amplified and changed to include inversions and phases unknown to, or not utilized by him. The system iron-graphite as the stable system, with iron-iron carbide metastable, is shown unnecessary. The completion of the Roozeboom diagram by the inclusion of the new phases Fe_6C and Fe_2C explains all the former discrepancies, and in addition brings into line a large mass of hitherto inexplicable and unconnected phenomena. The cast irons and their constituents become rational.

The phases Fe_6C, Fe_3C and Fe_2C are probably indistinguishable from each other in ordinary microscopic work.

A pearlite structure in cast irons may not be a pearlite at all, but a partially decomposed supersaturated solid solution from rapid cooling of the melt; the determination will depend on the previous heat treatment history of the piece. "Temper-carbon" is explained, and the conditions of its occurrence outlined.

The diagram may be still incomplete in one way—there is possibly a fourth allotropic form of iron, stable above 1200° C. This is indicated by the magnetic work of Curie; by structural changes in the iron (private communication to the author by E. S. Shepherd, of the U. S. Geophysical Laboratory); and possibly by a break in solidus and liquidus curves in the determinations of Carpenter and Keeling. I do not consider that there is as yet enough knowledge on this point to justify the mapping of a field for δ iron.

In the detail of the diagram, Fig. 11, the selections of the concentrations for the boundary points of the upper and lower limits of the γ + graphite field have been explained above in the discussion of Fig. 10; of the concentration at the solid eutectic in the discussion of Fig. 12. A slight change was also made in the size of the $\alpha + \gamma$ and $\beta + \gamma$ fields, making them larger than in Roozeboom's diagram. The selections of the temperatures for the various inversions have been based on the data of Carpenter and Keeling, with occasional allowances for supercooling. These temperatures I believe to be nearly correct. Looking back to Fig. 2 for the cooling curve data, the liquid eutectic line seems to be at a temperature of 1120° at its left end, and rise toward 1145° as it goes to the right. The supercooling would be least at the eutectic point. Therefore, I have put 1145° as the true temperature of the liquid eutectic. The horizontal line at the lower edge of the γ + graphite field was put by Roozeboom at 1000° C simply because he had no definite data for its real temperature, and 1000° was as good a place as any other. The inversion here has a comparatively small heat effect, and is therefore readily supercooled. The temperatures found for the inversion by Carpenter and

Keeling ranged from 1040° to 1090°. I have chosen 1090° as the most probable true value from the data. A similar argument holds for the Fe_3C breakdown which I have put at 800°. The data run from 775° to 800°; the heat effect is small, and supercooling consequently easy. The temperature assignment most likely to cause comment is that of 725° for the inversion γ solution $\rightleftarrows \alpha + Fe_3C$. Happily, here Carpenter and Keeling made determinations by both heating and cooling curves; the mean of these comes to 724°, with the values on heating curves 728°. On cooling curve determinations alone, the inversion began at higher temperatures with increasing carbon, the values being around 700° with low carbon and running up to 715° to 720° with 3 percent or more. 725° seems at present a good value for the temperature at which the inversion may be expected to begin in either heating or cooling, with a decently slow rate of change of temperature (not over 5° C per minute). For the $Fe_3C \leftrightarrows Fe_2C$ inversion 615° was chosen just as 800° and 1090° were picked out for the inversion above.

Most of these details are at present a matter of judgment, and the diagram may receive slight corrections in both temperatures and concentrations as more exact data are found. In view of the fact that the temperature of maximum rate of change is often put down as the temperature of an inversion, I should state that what physical chemistry accepts as the temperature of an inversion is that temperature at which the phases normal on both sides of the inversion can coexist indefinitely. As the temperature rises or falls away from the inversion temperature, one phase or the other becomes unstable and tends to disappear. Its instability and tendency to disappear, and therefore—other things remaining equal—its reaction rate, increase with the distance from the inversion temperature. Other things, however, do not remain equal. With lowering temperature, molecular freedom is rapidly lessened, and this curbs the reaction. Ordinary cooling curve determinations of inversions are then subject to *supercooling*; the temperature is carried more or less below the inversion temperature before the rate of heat evolution from the reaction is large enough to be detected. *Superheating* is far less likely to occur; ordinarily it may be said hardly to occur at all. The reason is that in heating, the test material is carried into a region of increased, instead of decreased, molecular freedom. Supercooling will be greater (1) the larger the cooling rate, (2) the smaller the amount of phases due to invert, (3) the less the specific heat evolution of the inversion. (2) and (3) are really identical effects, but from different causes. These considerations were kept in mind in choosing from the Carpenter and Keeling data the temperatures for inversions for Fig. 11.

The paper may be summarized as follows: It is an attempt to correlate and explain by a single rational diagram all iron-carbon alloys. It was shown by the work of Carpenter and Keeling that there occurred in these alloys two new inversions, and therefore two new phases, which had been unknown to, or unused by, Roozeboom in his discussion of the relations of iron and carbon. The probable identity of these new phases has been shown, by various methods of approach in each case, to be two new chemical compounds of carbon and iron, Fe_6C and Fe_4C. The temperatures and concentrations of the amplified Roozeboom diagram, including these new phases, have been indicated with a fair amount of accuracy. It has been shown that these new phases, together with a structure which is not a true phase, the partially decomposed frozen melt, explain and account for all the puzzling phenomena of the cast irons, phenomena which have led many investigators to believe that iron and carbon had a double equilibrium, one metastable and one stable system.

Temper-carbon is explained, and its amount and the conditions of its occurrence outlined. Incidentally, the white, or chilled irons, and the process of malleableizing are discussed, and a theoretical basis is furnished in agreement with the facts. There is room for research here as to the possible segregation of the silicon during malleableizing.

A contribution to the vexatious problem of the commercial cast irons is made by the determination and use of "displacing powers" for silicon, phosphorus, manganese, and sulphur. One other factor in the production of graphite, the effect of varying material of molds and size of castings on the cooling rate, and through the cooling rate the effect of these variables on the graphite, is not gone into quantitatively, on account of deficiency of data. The mechanical properties of the cast irons also vary considerably with the crystal or grain size, which is a function of the cooling rate. The low values placed on the effects (low displacing powers) of phosphorus and sulphur are certain to cause comment. As to this I would say that most of the current ideas about the effects of phosphorus and sulphur come from the changes these cause in the composition and temperature of the melt in the furnace. Both phosphorus and sulphur tend to decrease the carbon and silicon content of the melt, and make for whiter irons thus indirectly through the changes in carbon and silicon. The phosphorus and sulphur content of ordinary castings has little to do with either the mechanical or chemical properties of the castings. In this view I find, to my pleasure, I am in harmony with W. J. Keep, who has done more rational experimenting with cast irons than any other man. Keep says that the current ideas as to the effects of phosphorus, sulphur and manganese are largely superstition. He places as by far the most important factors (1) the carbon content, (2) the silicon content, (3) the cooling rate. By the finding and use of the displacing powers, the only variable left for determination is the cooling rate; if its effects be found, the making of cast irons will be at last on a rational and scientific instead of an empirical basis.

My thanks are due to Professor Bancroft and Mr. E. S. Shepherd for my training in metallography; to Professor Bancroft and W. S. Rowland for criticism and aid in this paper and its conclusions.

TABLES OF DISPLACING POWERS.

Data of Max Orthey, in *Metallurgie*, 7, 199 (1907).

Si	Mn	P	S	Total C	Combined C
I. Silicon-carbon					
2.34	0.54	0.56	0.064	3.57	0.49
2.13	0.60	0.55	0.061	3.49	0.40
1.96	0.57	0.50	0.069	3.46	0.52
1.72	0.49	0.54	0.072	3.42	0.59
1.63	0.51	0.56	0.083	3.40	0.75
1.42	0.56	0.52	0.095	3.52	0.80
1.20	0.55	0.50	0.116	3.43	0.83
0.97	0.52	0.59	0.146	3.37	0.89
II. Manganese-carbon					
1.36	0.35	0.49	0.076	3.27	0.74
1.42	0.50	0.52	0.080	3.36	0.73
1.46	0.70	0.50	0.082	3.40	0.72
1.32	0.85	0.56	0.075	3.62	0.81
1.27	1.00	0.55	0.067	3.56	0.83
1.24	1.26	0.49	0.070	3.49	0.84
1.28	1.39	0.48	0.062	3.54	0.82
1.29	1.56	0.52	0.057	3.64	0.81
III. Phosphorus-carbon					
1.31	0.52	1.43	0.090	3.48	0.74
1.37	0.56	1.25	0.084	3.54	0.81
1.24	0.53	1.07	0.075	3.49	0.79
1.27	0.62	0.90	0.082	3.46	0.83
1.38	0.50	0.71	0.074	3.44	0.79
1.32	0.46	0.49	0.062	3.50	0.76
1.42	0.57	0.24	0.073	3.53	0.79
1.34	0.71	0.96	0.070	3.45	0.81

TABLES OF VALUES OF GRAPHITE AND "EQUIVALENT TOTAL CARBON"

Sources of data are indicated as follows:

L = Ledebur, *Handbuch der Eisenhüttenkunde.*
Hi = Hiorns, *Iron and Steel.*
Ho = Howe, *Metallurgy of Steel.*
W = Wüst, article in *Iron and Steel Mag.*, March, 1906.
CK = Carpenter and Keeling, article in *Iron and Steel Mag.*, June, 1904.
P = Phillips and Bauerman, *Metallurgy.*

IV. Nearly pure iron-carbon alloys

Source	Si	C=⊂=Si	T. C.	=⊂= T. C.	G. C.	Mn	P	S	Kind of iron; remarks
W	0.02	0.01	2.56	2.57	0.00	0.02	0.04	0.01	These irons were all furnace-cooled; used in taking cooling-curves.
W	0.02	0.01	3.37	3.38	0.02	0.02	0.04	0.02	
W	0.02	0.01	3.56	3.57	0.01	0.02	0.04	0.01	
W	0.02	0.01	3.71	3.72	0.03	0.02	0.04	0.02	
W	0.01	0.00	3.81	3.81	0.02	0.02	0.04	0.01	
W	0.02	0.01	3.29	3.30	0.05	0.02	0.04	0.01	
W	0.01	0.00	2.94	2.94	0.04	0.02	0.04	0.01	
W	0.05	0.02	2.98	3.00	0.02	0.02	0.04	0.02	
W	0.04	0.02	3.52	3.54	0.13	0.02	0.04	0.22	
W	0.04	0.02	3.66	3.68	0.51	0.01	0.04	0.02	
W	0.04	0.02	2.99	3.01	0.01	0.02	0.04	0.02	
W	0.01	0.00	3.02	3.02	0.37	0.02	0.04	0.02	
W	0.03	0.01	2.65	2.66	0.00	0.02	0.04	0.02	
W	0.02	0.01	4.04	4.05	2.49	0.02	0.04	0.01	
W	0.04	0.02	4.04	4.06	1.75	0.02	0.04	0.01	

TABLES OF VALUES OF GRAPHITE AND "EQUIVALENT TOTAL CARBON"

IV. Nearly pure iron-carbon alloys—(*Continued*)

Source	Si	C=⊂=Si	T. C.	=⊂= T. C.	G. C.	Mn	P	S	Kind of iron; remarks
W	0.01	0.00	3.76	3.76	2.33	0.02	0.04	0.02	These irons were all furnace-cooled; used in taking cooling curves
W	0.01	0.00	4.82	4.82	3.31	0.02	0.04	0.02	
W	0.01	0.00	4.66	4.67	3.22	0.02	0.04	0.02	
W	0.11	0.05	3.94	3.99	2.28	0.02	0.04	0.02	
W	0.01	0.00	3.79	3.79	2.24	0.02	0.04	0.02	
CK	0.09	0.04	1.85	1.89	0.00	(Trace)	(About 0.02)	(About 0.02)	
CK	(About 0.06)	0.04	1.97	2.01	0.00				
CK		0.04	2.12	2.16	0.00				
CK		0.04	3.03	3.07	0.00				
CK		0.04	3.42	3.46	1.80				
CK		0.04	3.51	3.55	1.38				
CK	0.06	0.03	3.87	3.90	2.14				
CK	(About 0.09)	0.04	3.29	3.33	0.14		0.02		

Figures in parentheses in CK data are supplied from averages of the series, the individual data being lacking.

TABLES OF VALUES OF GRAPHITE AND "EQUIVALENT TOTAL CARBON"

V. Analyses of Commercial Irons

Source	Si	C=⊃=Si	T. C.	=⊃=T.C.	G. C.	Mn	P	S	Remarks
P	3.50	1.58	3.50	5.08	3.30	*1.58*	0.98	0.02	No. 1 foundry
P	1.79	0.81	2.81	3.62	2.16	0.56	*1.80*	0.10	No. 3 foundry
P	2.20	1.00	4.09	5.09	3.85	1.15	0.10	0.05	No. 1 bessemer
P	0.97	0.43	3.92	4.35	2.17	0.19	0.05	0.12	Forge
P	2.20	1.00	3.55	4.55	3.20	*6.70*	0.30	0.08	Manganiferous
Ho	1.96	0.88	2.18	3.06	1.62	0.60	0.28	0.03	—
Ho	2.51	1.14	1.87	3.01	1.19	0.75	0.26	0.05	—
Ho	2.96	1.33	2.23	3.56	1.43	0.70	0.34	0.04	—
Ho	3.92	1.77	2.01	3.78	1.81	0.84	0.33	0.03	—
Ho	4.74	2.13	2.03	4.16	1.66	0.95	0.30	0.05	—
Ho	5.13	2.31	3.38	5.69	2.59	0.77	1.12	0.17	—
Ho	5.13	2.31	3.39	5.70	2.68	0.56	1.12	0.23	—
Ho	5.47	2.45	2.88	5.33	2.88	*1.54*	0.60	0.04	—
Ho	5.92	2.67	2.96	5.63	2.38	1.09	0.60	0.04	—
Ho	0.19	0.09	1.98	2.07	0.38	0.14	0.32	0.05	—
Ho	0.45	0.20	2.00	2.20	0.10	0.21	0.33	0.05	—
Ho	0.96	0.43	2.09	2.52	0.24	0.26	0.33	0.04	—
P	0.40	0.18	1.57	1.85	1.10	0.44	*1.62*	0.30	Forge
Hi	0.20	0.09	3.92	4.01	0.12	0.55	0.33	0.22	White
L	1.23	0.55	3.51	4.01	0.75	*3.36*	0.89	0.05	Mottled
L	1.03	0.47	3.67	4.14	2.46	*2.74*	0.09	0.05	Mottled
L	0.88	0.40	5.20	5.60	2.71	*4.47*	0.67	0.04	Gray spiegel
Hi	3.34	1.51	4.02	5.52	3.44	0.41	1.11	0.02	No. 3 gray
Hi	3.36	1.52	2.96	4.48	2.46	0.36	0.90	0.01	No. 3 gray

TABLES OF VALUES OF GRAPHITE AND "EQUIVALENT TOTAL CARBON"

V. Analyses of Commercial Irons—(*Continued*)

Source	Si	C =⊂= Si	T. C.	=⊂= T.C.	G. C.	Mn	P	S	Remarks
Hi	2.24	1.01	3.75	4.76	3.50	0.27	1.58	0.05	No. 3 gray
Hi	2.80	1.27	2.77	4.04	2.74	0.28	1.55	0.03	No. 3 gray
Hi	2.90	1.31	3.55	4.86	3.40	0.31	1.56	0.04	No. 3 gray
Hi	2.71	1.23	3.02	4.25	2.95	0.34	1.64	0.03	No. 3 gray
Hi	0.82	0.37	3.94	4.31	3.06	0.78	0.23	0.02	Charcoal pig
Hi	0.75	0.34	4.10	4.44	2.90	0.66	0.25	0.03	Charcoal pig
Hi	0.63	0.28	4.30	4.58	2.42	0.53	0.27	0.04	Charcoal pig
Hi	0.66	0.30	4.47	4.47	2.90	0.31	0.24	0.04	Charcoal pig
Hi	2.85	1.28	3.70	4.98	3.52	1.31	0.03	0.03	No. 1 gray
Hi	2.40	1.13	3.50	4.63	3.10	0.40	0.04	0.04	No. 3 gray
Hi	2.60	1.17	3.65	4.82	3.40	1.24	0.03	0.04	No. 2 gray
Hi	1.10	0.50	3.21	3.71	2.16	0.33	0.04	0.48	Mottled
Hi	1.78	0.80	3.80	4.60	2.60	0.13	0.04	0.02	Bessemer
Hi	4.89	2.20	3.65	5.85	3.44	0.84	0.06	—	Silicon pig
L	5.32	2.40	2.46	4.86	2.25	2.52	0.48	0.01	Silicon pig
L	4.37	1.97	2.74	4.71	2.64	0.71	—	—	No. 3 gray
L	3.50	1.57	3.42	4.99	3.27	0.79	0.96	0.01	No. 3 gray
L	3.50	1.57	3.50	5.07	3.30	1.58	0.98	0.02	No. 1 gray
L	2.77	1.25	3.78	5.03	3.33	1.31	0.80	0.02	No. 1 gray
L	2.16	0.97	2.82	3.79	2.54	0.67	0.51	—	No. 3 gray
L	2.93	1.32	3.86	5.18	3.40	1.62	0.75	0.04	No. 1 gray
L	2.25	1.01	4.15	5.16	3.25	1.25	0.05	0.02	No. 1 gray
L	2.52	1.14	3.52	4.66	3.39	0.68	1.49	0.05	No. 3 gray
L	1.95	0.88	3.58	4.46	2.55	1.05	0.05	0.04	No. 2 gray

TABLES OF VALUES OF GRAPHITE AND "EQUIVALENT TOTAL CARBON"

V. Analyses of Commercial Irons—(*Continued*)

Source	Si	C⟺Si	T. C.	⟺T.C.	G. C.	Mn	P	S	Remarks
L	1.75	0.78	3.47	4.25	1.95	0.95	0.05	0.06	No. 3 gray
L	1.55	0.70	3.23	3.93	1.15	0.65	0.04	0.07	No. 4 gray
L	1.45	0.65	3.02	3.67	0.85	0.58	0.05	0.08	No. 5 forge
L	2.71	1.22	3.82	5.04	3.30	0.59	*1.78*	—	No. 3 gray
L	2.86	1.29	3.71	5.00	3.40	0.56	*1.89*	—	Light gray
L	1.87	0.84	3.76	4.60	3.10	0.51	*1.85*	—	Light gray
L	2.29	1.03	3.76	4.79	3.10	0.59	*1.86*	—	Mottled
L	3.31	1.50	4.76	5.26	4.00	*3.41*	0.07	0.02	Gray bessemer
L	2.52	1.13	3.76	4.89	3.10	*3.90*	0.07	0.03	Gray bessemer
L	1.73	0.77	3.14	3.91	2.97	*3.78*	0.08	0.02	Gray bessemer
L	2.11	0.96	3.61	4.57	3.01	0.47	0.46	0.04	Dark gray
L	1.35	0.61	3.78	4.39	3.07	*2.52*	0.03	0.05	Gray
L	1.79	0.80	3.01	3.81	2.26	*2.33*	0.03	0.04	Mottled
L	2.20	1.00	3.50	4.50	2.97	0.41	0.51	0.07	Gray
L	1.68	0.76	2.93	3.69	2.53	0.35	0.54	0.07	Mottled
L	1.02	0.46	3.19	3.65	2.40	0.28	0.59	0.09	Strongly mottled
L	0.70	0.32	3.21	3.53	1.63	0.14	0.56	0.14	Light gray
L	1.48	0.66	3.50	4.16	2.35	*2.44*	0.12	0.05	Gray
L	1.76	0.79	2.73	3.52	2.23	1.42	0.36	0.12	Light gray
L	2.54	1.15	2.52	3.67	1.78	*2.88*	0.15	0.04	Mottled
L	2.24	1.01	3.68	4.69	2.88	0.17	0.11	0.01	Gray
L	0.63	0.28	2.70	2.98	2.26	0.32	Trace	0.15	Mottled
—	2.42	1.09	3.39	4.48	2.73	1.09	0.31	0.04	—
—	1.88	0.85	3.34	4.19	2.54	0.44	0.30	0.10	—
—	1.16	0.52	3.36	3.88	2.08	0.36	0.30	0.20	—

Cornell University,
May, 1908.

ELECTROLYTIC CORROSION OF BRASSES IN SYNTHETIC SEA WATER

BY A. T. LINCOLN AND G. C. BARTELLS, JR.

In a previous paper[1] there was presented the results of our investigation on the electrolytic corrosion of brasses in normal solutions of a number of simple salts, including sodium chloride, sodium sulphate, sodium acetate, sodium nitrate, sodium carbonate, ammonium nitrate, ammonium oxalate and acid ammonium oxalate. It was our intention to determine the corrosion in solutions of mixtures of various salts and particularly in sea water. In this paper we shall present the results obtained in the electrolytic corrosion of a number of brasses in synthetic sea water and in solutions of commercial bath salt.

The brasses employed were those prepared for the previous work and represented practically all of the stable solid solutions of copper-zinc alloys at 400° C, at which temperature they were annealed for several weeks, in order to insure equilibrium of these phases. For the preparation of these brasses, as well as for the details of the method employed in carrying out the electrolytic corrosion, reference must be had to the previous articles.[2]

In general, the method consisted in arranging the thirteen test pieces so that they could be corroded simultaneously. The brasses were the anodes and were rotated about 800 revolutions per minute, thus keeping the electrolyte thoroughly mixed. A current of about 0.03 ampere was passed through the solutions for about six to seven hours, and two copper coulometers were placed in series, and from these the current employed was ascertained. Platinum cathodes were used.

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[1] Trans. of the Amer. Elec. Chem. Soc., 11, 43 (1907). Jour. Phys. Chem. 11, 501 (1907).

[2] l. c.

Corrosion in Bath Salt Solution *

Solutions of commercial West India bath salt were prepared of approximately the concentration of sea water, *i. e.*, about 3.5 percent solution. The corrosion was run in triplicate and the data presented in Table 1 are characteristic. In the first column is given the percentage of copper in the test pieces; in the second column the number of grams the test pieces lost during corrosion; in the third column, the number of grams of copper in the corrosion product; in the fourth, the percent of copper found is of the total corrosion; while in the last column is given the so-called current efficiency, *i. e.*, the percent of copper and zinc dissolved was of the quantity that should have been dissolved by the current that was used.

TABLE 1

Percent Cu in test pieces	Gram of corrosion	Gram Cu in corrosion	Percent Cu in corrosion	Current efficiency
3.08	0.2155	0.0017	0.8	92.0
10.5	0.2096	0.0034	1.6	89.1
22.6	0.2083	0.0050	2.5	87.8
47.6	0.2026	0.0125	6.7	84.4
51.3	0.2565	0.0654	25.9	96.3
56.8	0.2827	0.0990	34.2	100.0
60.3	0.3302	0.2055	62.3	98.7
66.5	0.3420	0.2287	66.9	98.9
73.4	0.3595	0.2718	75.6	97.5
76.3	0.3664	0.2838	77.4	98.0
83.3	0.3901	0.3295	84.4	98.5
86.6	0.4019	0.3525	87.7	98.7
93.6	0.4249	0.4003	94.1	98.7

Copper deposited in coulometer = 0.2269 gram.

These results are represented diagrammatically in the figure by the curves designated Bath Salt. The amount of corrosion decreases with the decrease of copper content until brasses of about 53 percent copper are reached, when the corrosion remains practically constant for the remainder. The curve representing the copper in the corrosion shows that the corrosion product from the brasses containing less than about 53 percent of copper consists practically of pure zinc. This accounts for the film of pure copper which appears on the 51.3 percent copper brass and which scales off readily. The percent of copper in the corrosion as represented in the next to the last column for the brasses containing α, β, and α and β crystals is practically the same as in the test pieces; but with the appearance of the γ solid solutions, the copper apparently ceases to dissolve and the corrosion consists almost exclusively of the solution of zinc. The current efficiency as given in the last column for the brasses high in copper, represents that the copper and zinc dissolve almost quantitatively. Where the corrosion consists chiefly of zinc, the current efficiency is low. The current efficiency is calculated upon the basis that the copper dissolves as cuprous copper and this has been confirmed in a series of experiments which we have carried out.

Corrosion in Synthetic Sea Water

According to Dittmar[1] the average of the total solids in the 160 samples of sea water collected by the Challenger expedition is 3.5 percent. He gives[2] the following average composition of the solids dissolved in sea water:

Chloride of sodium	77.758
Chloride of magnesium	10.878
Sulphate of magnesium	4.737
Sulphate of lime	3.600
Sulphate of potassium	2.465
Bromide of magnesium	0.217
Carbonate of lime	0.345
Total solids	100.000

This combination of acids and bases is an arbitrary one and in the preparation of our sample of synthetic sea water, the same combinations were retained except that the car-

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[1] Geol. History of Lake Lahontan, U. S. G. S. Monograph, XI, Russel, p. 178.

[2] The Voyages of H. M. S. Challenger: Physics and Chem., 1, 204.

bonate was potassium carbonate instead of calcium carbonate, while the calcium was introduced as additional calcium sulphate, the potassium required for the potassium carbonate being deducted from the potassium sulphate and the calcium sulphate substituted. Otherwise the sample of sea water was prepared by employing the salts listed, and the quantities taken sufficient to make a solution containing 3.5 percent of solids, the concentration of sea water.

The electrolytic corrosion was carried out in the manner previously described, and the data given in Table 2 are the results of one of the duplicate determinations. The headings of the columns are the same as in the other tables and are self-explanatory.

TABLE 2

Percent Cu in test pieces	Gram of corrosion	Gram Cu in corrosion	Percent Cu in corrosion	Current efficiency
3.08	0.2140	0.0009	0.45	92.2
10.5	0.1858	0.0012	0.65	80.0
22.6	0.2057	0.0015	0.73	88.6
47.6	0.2118	0.0031	1.5	90.8
51.3	0.2513	0.0405	16.1	100.0
56.8	0.3040	0.1428	46.9	101.4
60.3	0.3295	0.2044	62.0	99.4
66.5	0.3424	0.2243	65.6	100.8
73.4	0.3619	0.2660	73.5	100.5
76.3	0.3679	0.2720	76.1	101.8
83.3	0.3917	0.3251	83.0	100.9
86.6	0.4020	0.3459	86.0	101.0
93.6	0.3485	0.3239	93.0	82.5

Copper deposited in coulometer = 0.2253 gram.

The curve marked Synthetic Salt No. 1 in the figure represents diagrammatically the data given in Table 2. These curves, as well as the others, have been smoothed and while no values were obtained for brasses of compositions between 47 and 22 percent copper, the curves have been drawn continuous.

Another series of corrosions was run in a synthetic sea water wherein iodine was substituted for bromine. The iodine was introduced as potassium iodide and the other necessary adjustments of the quantities of the constituents calculated so that a 3.5 percent solution was prepared. The data obtained from the results of these corrosions in this solution are represented by the series given in Table 3.

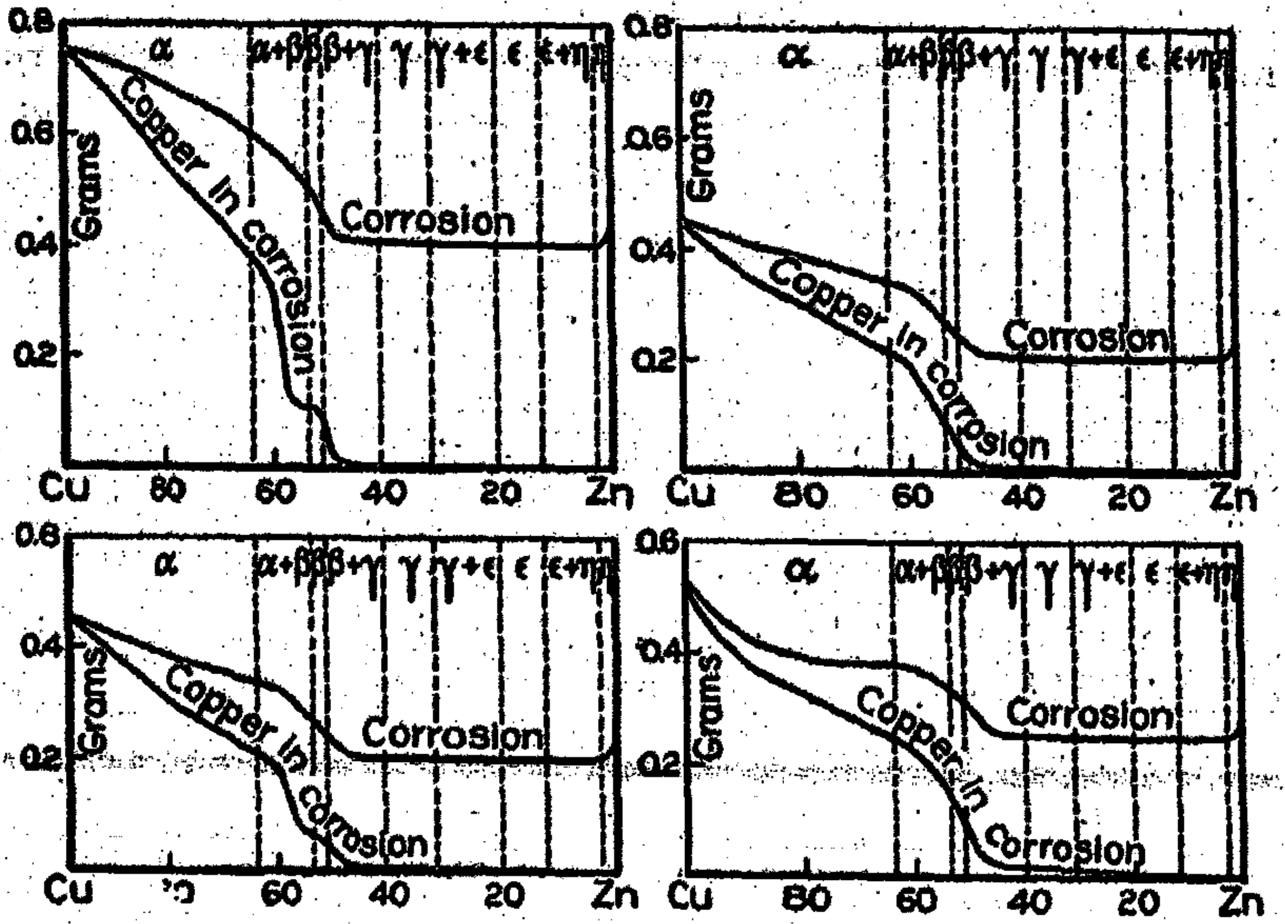
TABLE 3

Percent Cu in test pieces	Gram of corrosion	Gram Cu in corrosion	Percent Cu in corrosion	Current efficiency
3.08	0.2647	0.0016	0.62	98.3
10.5	0.2173	0.0028	1.3	80.4
22.6	0.2538	0.0083	3.5	93.1
47.6	0.2613	0.0260	9.9	86.6
51.3	0.3488	0.1438	41.2	103.8
56.8	0.3535	0.1888	53.6	97.5
60.3	0.3804	0.2420	63.6	97.9
66.5	0.3774	0.2520	66.8	95.0
73.4	0.3781	0.2845	75.3	89.3
76.3	0.3805	0.2835	76.6	90.4
83.3	0.4081	0.3450	84.5	89.5
86.6	0.4092	0.3585	87.6	87.5

Copper deposited in coulometer = 0.2612 gram.

The curves labeled Synthetic Salt No. 2 represent diagrammatically, as do the other curves, the relation of the grams of corrosion, the grams of copper in the corrosion product and the variation of these with the change in the concentration of the brasses. The vertical dotted lines represent the boundaries of the different solid solutions.

The upper curve in these diagrams represents a decrease in the amount of corrosion with the decrease in the copper content of the brasses. In some of the determinations there seemed to be a tendency for the amount of corrosion of the sample of brass of the highest copper content to be lower than that found for brasses of lower copper content. In order to determine whether this was real or not, a number of determinations of the amount of corrosion of the three highest copper brasses were made in the two synthetic salts and the



Upper figure, left: Sodium Chloride.
Upper figure, right: Synthetic Sea Salt, No. 1.
Lower figure, left: Bath Salt.
Lower figure, right: Synthetic Sea Salt, No. 2.

bath salt. The data given in Table 4 represents the results of these numerous determinations.

TABLE 4

Percent Cu in test pieces	Gram of corrosion		
	Synthetic salt No. 1	Synthetic salt No. 2	Bath salt
93.6	0.3681	0.3564	0.3713
86.6	0.3613	0.3483	0.3448
83.3	0.3460	0.3447	0.3379

These values show conclusively that the amount of corrosion increases with the increase in the copper content of the brass.

In the figure the curves for the corrosion of the brasses as determined in normal sodium chloride solutions are given for comparison. It will be readily observed that the general form of the curve representing the grams of corrosion in the sodium chloride solution is the same as that for the synthetic sea waters and for the bath salt solutions. The curve representing the grams of copper in the corrosion product is similar in all four cases. With the appearance of γ crystals, the copper in the corrosion product drops nearly to zero; and for the brasses, the copper content of which is less than about 53 percent copper, the corrosion product is practically pure zinc. Therefore, we may conclude that the corrosion of these samples of brasses is practically the same in the synthetic sea water and in solutions of bath salt as in pure sodium chloride solutions.

Urbana, Illinois,
May 21, 1908.

NEW BOOKS

The Metallurgy of Iron and Steel. *By Bradley Stoughton. 15 × 24 cm; pp. vi + 509. New York: Hill Publishing Company, 1908. Price: bound, $3.00.*—As the preface says, the book is intended for use as "a text not only for college work, but for civil, mechanical, electrical, metallurgical, mining engineers and architects, and for those engaged in work allied to engineering or metallurgy."

The book is very readable and well printed. The many drawings and diagrams are clear and the photographs of various plants, furnaces, machines and so forth illustrate the text very admirably. As a whole the work is a very creditable addition to the English literature on the subject.

The author first takes up the location and kinds of iron ore, the methods of mining and transportation from the mines to the furnaces, and gives a very clear treatment of the blast furnace process with its reactions and charge calculations. In the next chapter there is a comparison of the different purification processes of pig iron and the following three chapters are devoted to the manufacture of crucible steel, wrought iron, and the Bessemer and open hearth processes. The defects in ingots and castings and the remedies for them are also dealt with.

The mechanical treatment of steel is then discussed and the different methods explained very nicely. This is followed with a very complete description of iron and steel founding.

At this point the author takes up the "solution theory of iron and steel," or rather the theory of the solution of carbon in iron and steel. He illustrates with the silver-gold and lead-tin alloys, the two different cases of crystallization generally met with, where pure crystals of one component or crystals of one component either combined with or dissolved in another component separate from the solution. The explanation is particularly clear and concise and could be understood by one having but little knowledge of physical chemistry. This is a forerunner to the discussion of the iron-carbon diagram, in which a very clear statement of the dividing line between iron and steel is given. The Roberts-Austin diagram as interpreted by Roozeboom is taken up briefly. There are some photomicrographs shown, including F. Osmond's pearlite picture, which has probably been used more than any other photomicrograph ever taken. The photomicrographs are not good but they are probably as good as the average which are published. They illustrate the appearance of phases as occurring in manufacture, but it is a question whether they really illustrate the phases which occur in the various fields of the diagram for the reason that the heat treatments have not been of sufficient duration to attain equilibrium. The effect of impurities in steel is treated.

A very good discussion of the heat treatment of steels is given and here the iron-carbon diagram is used to show to just what temperatures heating should be carried to obtain the best results and how overheating may be corrected. This is illustrated by photomicrographs of a medium quality.

Alloy steels, with a description of their manufacture, their properties and the present theory accounting for them, the corrosion of iron and steel and the electrometallurgy of iron and steel are each given a chapter.

The last chapter of the book is an elementary treatment of the physics and chemistry which are essential to the proper understanding of the manufacture of iron and steel. It is very well written, and with the exception of a few minor misstatements furnishes an excellent introduction for the practical man who knows the methods of the various processes, but is a bit lacking in the fundamental principles.

There is a diagram of a coke oven retort printed upside down, but the book as a whole is very free from typographical errors. A translation, which is a common mistake, of "Mischkrystallen" is given as mixed crystals while it really means crystals of a mixture of two or more components in solution in or combined with one another.

At the end of each chapter there is given a bibliography of works upon the subject discussed in the chapter. These are numbered and reference is made to the numbers from time to time throughout the book. However, to find the reference, one has to run through the chapter ends. It would have been more convenient if the entire list of references had been placed together.

The book is a very good presentation of the subject, especially for the beginner. The tables for furnace charges, of analyses and of physical tests show a large amount of work which is of great value. The book is well printed on good paper and well worth its price. *W. S. Rowland*

Lead Refining by Electrolysis. *By Anson Gardner Betts. First Edition. 15 × 23 cm; pp. ix + 394. New York: John Wiley & Sons. London: Chapman & Hall, 1908. Price: $4.00 net.*—In the preface the author says:

"The electrolytic refining of lead bullion has now become an established metallurgical process, with further extensions confidently expected to come from time to time. Lead is almost an ideal metal to refine electrolytically, because its electrochemical equivalent is very high, and hence the power cost is small, and the depositing tanks are relatively smaller or fewer than for other common metals. Its casting into anodes is especially easy, and it stands high enough in the electrochemical scale to leave its impurities almost entirely in the anode slime, as metals; so there is no appreciable contamination of the electrolyte.

"The contained information is the result of a number of years of study, experiment and practical work, and is published in the hope that it will save those who may be interested in lead refining practice or its improvement the repetition of experiments already performed, and give them the benefit of the work already done by others and myself. Some space has been devoted to theoretical discussions of conductivity of electrolyte, etc., which I thought would be useful and instructive."

The headings of the chapters are: electrolytes for lead refining; chemistry of slime treatment; deposition of antimony from the fluoride solution; electrolytic refining of doré bullion; the manufacture of hydrofluoric and fluosilicic acids; choice of constants; refinery construction, operation, and refining costs; products; treatment of lead containing by-products, analytical methods and experimental work; bibliography. There are also three appendices: plant of the Consolidated Mining and Smelting Company of Canada, Limited, at Trail, British Columbia; lead refining plant of the United States Metal Refining Company at Grasselli, Lake County, Indiana; treatment of lead refinery slime with solution of ferric fluosilicate and hydrofluoric acid.

This is a book which should be in the library of every one interested in electrochemistry. It is of course an authoritative work on electrolytic lead refining and valuable as such. It is a good deal more than that, however. The author has apparently written it direct from his note-books, and he has included a large number of minor experiments and details which are very interesting regardless of whether they chronicle successes or failures. The book is a good one and it is to be hoped that some day we may have more of the same type. *Wilder D. Bancroft*

A Treatise on Chemistry. *By H. E. Roscoe and C. Schorlemmer. Volume II. The Metals. New Edition, Completely Revised by H. E. Roscoe and A. Harden. 14 × 22 cm; pp. xii + 1436. New York: The Macmillan Company, 1907. Price: $7.50 net.*—In the preface to this edition, Sir Henry Roscoe says:

"Much new and important matter with regard to the metals and their compounds has come to light in the ten years since the last edition of this work appeared and in the present volume care has been taken to include all the more important points connected with the recent discoveries. The subject of crystallography, which formerly appeared in the first volume, has now been included in the second, and here I must express my thanks to Professor Miers for permitting the use of the illustrations from his own work and for reading the proof of this chapter. Several contributors have assisted in the work of revision; amongst them I must mention Mr. C. O. Bannister, who has written upon Metallurgy and Alloys, Mr. Harry Baker, Dr. Colman, Dr. Marshall Watts, and Mr. Young, who have all assisted in various departments."

In this volume the metals of the eight groups are taken up and there is a special chapter on the radioactive metals. The general plan of the book is that of the earlier editions, but the newer work has been incorporated in a very satisfactory manner. Thus we find Tilden's work on specific heats, p. 24; Werner's theory of principal and supplementary valences, p. 37; J. J. Thomson's work on the properties of the model atom, p. 41; Mendeléeff's hypothesis in regard to the ether, p. 71; the behavior of binary alloys, p. 78; the phase rule, p. 115; the mass law, p. 132; the Castner sodium process, p. 242; the electrolytic process for making chlorate, p. 329; Bredig's work on colloidal gold, p. 500; Hall's process for making aluminum, p. 701; and many other matters too numerous to cite.

In most cases the new matter is correct; but there is an occasional slip, as in the following passage, p. 830:

"The alloys corresponding in composition to the formulae $SnCu_3$ and $SnCu_4$ are definite chemical compounds, and are the only ones of the series which remain homogeneous after melting, a certain amount of liquation taking place in all the others." As a matter of fact, liquation takes place with both these alloys and $SnCu_4$ is not a compound.

The last page of the volume is so interesting that I quote it in full, omitting the foot-notes, however.

"The discovery that the atoms of certain elements undergo continuous spontaneous disintegration with formation of substances of lower atomic weight necessitates a profound modification of the conception of the chemical atom which has hitherto been accepted. The corpuscular theory of matter has paved the way for such a modification by regarding the atom as containing a number of electrons, although recent work indicates that the number of these present in an atom is much smaller than was at first thought and is of the order of the number expressing the mass of the atom in multiples of that of hydrogen.

"The atom must now be regarded as an aggregate of simpler forms of matter, possessing enormous potential energy. This aggregate may, under conditions which we are not yet able to control, break into simpler forms, a large amount of energy being evolved in the change. Hence the idea of the unalterability of the atom postulated by Dalton must be modified, and the atom must be regarded as a complex, but of a higher order than the chemical compounds formed by the union of atoms with each other. It is impossible at present to establish a more precise characterization of this higher order of complex substances than is expressed in the statement that the decomposition of the atom is beyond our control, and that the energy changes are of a higher order of magnitude than is the case with ordinary compounds.

"These discoveries, however, whilst opening out new views as to the constitution of matter, are in no degree inconsistent with the well-established facts of chemical combination or with the application to them of Dalton's atomic theory." *Wilder D. Bancroft*

Introduction to Metallography. *By Paul Goerens. Translated by Fred Ibbotson. 15 × 23 cm; pp. x + 214. New York: Longmans, Green & Co., 1908. Price: $2.50 net.*—The book opens with a description of the methods of determining cooling curves. Next we have the application of the phase rule to aqueous solutions, fused salts, and alloys. This is followed by a chapter on the microscopic study of alloys. The book closes with a chapter on the metallography of the iron-carbon alloys. Most of the book dates from 1906 and therefore does not include the more recent work on alloys. In consequence there is not enough stress laid on the importance of annealing until equilibrium is reached. Carborundum does not seem to be referred to anywhere in the book though as a grinding material it is far superior to emery.

The descriptions of methods are good and should prove serviceable to those interested in metallography. The translation is good as a rule, though such expressions as 'the springing of a tube,' 'the gap of solubility,' and 'the stable system may eventuate,' are not satisfactory. The zinc-antimony diagram, p. 79, is defective. It seems to the reviewer that some reference should have been made to electromotive force determinations as a method of identifying alloys. The good and the poor points of the book are all due to the same thing, that the author is really interested in the iron-carbon alloys alone. All the rest is perfunctory. The book is an introduction to the study of carbon steels. Considered as such, it is a good book. As it is the only book, it is of value no matter what one's point of view may be. *Wilder D. Bancroft*

THE ACTION OF CARBON DIOXIDE UNDER PRESSURE UPON A FEW METAL HYDROXIDES AT 0° C[1]

BY F. K. CAMERON AND W. O. ROBINSON

Introduction

The coloring matter of soils consists of a film of colored oxides, hydroxides, and organic matter adhering to, and surrounding the mineral particles. Practically all this adhering material has been deposited from solution, and to explain the solution, transportation and deposition of its constituent oxides of ferrous and ferric iron, manganese, calcium, magnesium and the like, it has been assumed generally that these bases form bicarbonates which readily change to carbonates and oxides with a diminishing pressure of carbon dioxide and with oxidation. In the investigation of the mechanism of this solution and redeposition of coating materials on soil grains, the action of carbon dioxide upon several hydroxides has been studied under pressures from 1 to 5 atmospheres, and for convenience the experiments have been carried out at the temperature of melting ice.

References to bicarbonates of lime, magnesia, ferrous oxide and manganous oxide appear quite generally in geochemical literature. A critical examination of the facts fail, however, to show any direct evidence of the existence of the above-mentioned compounds as solids. Their existence in solution has been assumed to account for the increased solubility of the carbonates, particularly those of lime and magnesia, in water containing dissolved carbon dioxide.

In general, the method used in the present investigation consisted in forcing a known amount of carbon dioxide into a small closed space containing the hydroxide under investigation and a known volume of water, and then measur-

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[1] Presented to the American Chemical Society, at New Haven, June 1908, by permission of the Secretary of Agriculture.

ing the pressure of the system after absorption had taken place. For this purpose the apparatus shown in Fig. 1 was employed.

A is a heavy separatory funnel containing mercury. *B* is a tube allowing the mercury to flow out of the tube *C*, till a constant level has been reached. Carbon dioxide is allowed to displace the mercury in the space *C* till the level of the tube *B* is reached. The pressure is adjusted to that of the atmosphere by means of a levelling tube *L*. *E* is a thick-walled tube in which the substance to be investigated was placed. During the progress of an experiment, *E* was surrounded by a beaker filled with a mixture of cracked ice and water. *F* is a glass tube closed at one end, around which a solenoid is wound. By alternately making and breaking a current through the solenoid, a small stirrer is agitated within the apparatus, the stirrer consisting of a platinum wire looped at one end and fastened to a small rod of soft iron at the other end.[1] The pressure is registered by the closed arm manometer *G*. The capacity of the apparatus was measured by absorbing and weighing several charges of

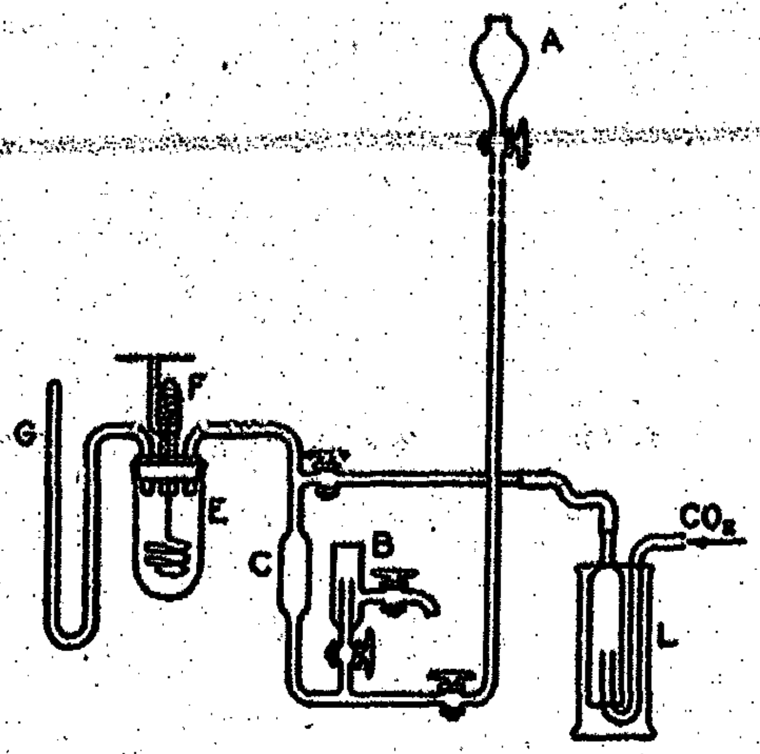

Fig. 1

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[1] As used by Kahlenberg, Jour. Phys. Chem., 10, 198 (1906).

carbon dioxide displaced by mercury and averaging the weight of the several charges. For instance, at 20°, five charges weighed 0.1196 gram, therefore one charge equals 0.0239 gram. In a second experiment, eight charges weighed 0.1920 gram, or 0.0240 gram per charge. The average weight per charge was found in this way to be 0.0240 gram. Later, after the original apparatus had been broken and mended, the weight of a single charge was 0.0140 gram for some series of experiments and 0.0158 in other series.

The experiments were carried out as follows: The space *C* was filled with mercury and the chamber *E* attached. Carbon dioxide was then allowed to flow into *C*, displacing the mercury to the level determined by the tube *B*. Then the proper stopcocks were closed and carbon dioxide forced into the chamber by the mercury from *A*. The contents of *E* were vigorously stirred till the manometer showed no decrease in pressure, when a final reading was taken and the operation repeated. The carbon dioxide used in these experiments was the ordinary commercial article. An examination of the gas showed it to contain less than 1 percent impurities, the impurities being almost entirely atmospheric air. As successive portions of carbon dioxide were forced into the tube *E*, the proportion of carbon dioxide in the gas phase constantly decreased. For the present investigation, however, this fact had no importance, since it was the nature of the solid phases which were being determined.

The results were interpreted by plotting the weight of carbon dioxide against the corresponding pressure in the chamber. It is evident, that when the carbon dioxide added entered the solid phase with the formation of a definite compound, no increase of pressure could have resulted. Hence a line perpendicular to the pressure axis would mean that a new definite compound is forming; a continuous curve not perpendicular to the pressure axis would mean either that there is no absorption of carbon dioxide in the solid phase, or that the latter consisted of a series of solid solutions; a break in the curve would indicate the disappearance of a solid phase. Finally, it should be observed that a curve perpendicular to the pressure axis corresponds to two solid phases being present, while a curve cutting the axis at an angle other than 90° corresponds to one solid phase being present.

Calcium Carbonates

The partial pressures of carbon dioxide above calcium carbonate at ordinary temperatures must be of vanishing importance, for that compound is stable in an atmosphere practically free from carbon dioxide.

Irvine[1] found that when carbon dioxide was passed through lime water, a precipitate was formed and heat was evolved; and when on the further passage of carbon dioxide the precipitate began to dissolve, heat was again given off till no more solid dissolved, at which point the temperature became constant. No precautions were mentioned regarding changes in temperature, and the entire rise in temperature was only 1.5° C. Irvine attributed the second raise in temperature to the formation of carbonic acid in solution rather than to the formation of calcium bicarbonate.

Schloesing[2] and Engel[3] found that the solubility of calcium carbonate in carbonated waters varied continuously with the partial pressure of carbon dioxide above the liquid, and proposed a formula showing the equilibrium between the pressure of carbon dioxide and dissolved carbonate which accords well with the data. Since the initial solid phase is calcium carbonate and the curve continuous, it follows that no other solid phase was formed.

Treadwell and Reuter[4] found that under pressures of one atmosphere, the solubility of calcium carbonate varied continuously with the pressure of carbon dioxide in the gas phase. They state that at 15° C and at a partial pressure of zero for carbon dioxide in the gas phase, the liquid held

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[1] Chem. News, 63, 192 (1891).

[2] Comptes rendus, 74, 1552 (1872).

[3] Ibid., 101, 949 (1885); Ann. Chim. Phys. (6), 13, 344 (1888).

[4] Zeit. anorg. Chem., 17, 170 (1898).

calcium oxide and carbon dioxide in quantities exactly corresponding to calcium bicarbonate.

Raikow[1] found that lime water absorbed enough carbon dioxide to form a bicarbonate in solution, making a correction for the solubility of carbon dioxide alone in water, and claimed that the carbon dioxide must be *in some way* bound chemically, for it could not be removed by mechanical means, but it was always present in the requisite amount.

Leavitt, in a paper before the Washington Chemical Society, described the formation of a solid bicarbonate of calcium by the addition of a solution of calcium chloride to a solution of ammonium bicarbonate at 0° C. The resultant solid was crystalline in appearance and decomposed violently at about 4° C. The analysis for calcium, though somewhat uncertain, indicated that the substance was calcium bicarbonate, although no determinations were made for carbon dioxide or water. Rammelsberg[2] found in a river rhomboidal crystals of $CaCO_3.5H_2O$ which gave up their water of crystallization at 15°. This and other crystalline hydrates have also been described by Pelouze,[3] Hunt,[4] and Tschiwinsky.[5] Since the percentages of lime in the pentahydrate and the bicarbonate are not far apart, an analysis for carbon dioxide would be necessary to confirm the existence of a bicarbonate.

The vapor pressure obtained in the present investigation by adding successive amounts of carbon dioxide to wet calcium carbonate are given in Table I, and when plotted give a curve approximating very closely a straight line, making a wide angle with the pressure axis. Consequently, no new solid carbonate is formed by the addition of carbon dioxide to wet calcium carbonate under vapor pressure of 4.5 atmospheres at the temperature of melting ice. The

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[1] Chem. Ztg., 28, 1247 (1904).

[2] Ber. d. chem. Ges. Berlin, 4, 569 (1871).

[3] Jour. Pharm. (4), 1, 278 (1865).

[4] Am. Jour. Sci. (2), 42, 49 (1866).

[5] Annuaire geol. et minéral. Russie, 8, 245 (1906).

weight of calcium carbonate used in this experiment was not determined, since such data would be of value only if a new carbonate had been formed.

TABLE I

Showing the vapor pressure of carbon dioxide over wet $Fe(OH)_3$, $Fe(OH)_2$, $CaCO_3$ and $Be(OH)_2$ at 0° C. Pressures in cm. Hg

Grams CO_2 added	Pressure over $Fe(OH)_3$	Pressure over $Fe(OH)_2$	Pressure over $CaCO_3$	Pressure over $Be(OH)_2$
0.0	76	76	76	76
0.014	85	76	84	87
0.028	99	76	96	100
0.042	117	76	113	114
0.056	132	76	127	132
0.070	148	76	143	142
0.084	165	86	158	161
0.098	179	102	174	178
0.112	195	118	189	191
0.126	207	134	205	205
0.140	224	152	220	219
0.154	240	168	235	241
0.168	254	183	251	253
0.182	273	199	268	271
0.196	287	214	283	284
0.210	303	229	299	299
0.224	318	245	314	317
0.238	334	259	330	330
0.252	350	274	346	346
0.266	368	—	—	—

This experiment was repeated three times, and there can be no doubt that with pressures less than 4.5 atmospheres of carbon dioxide no other than normal carbonate or a hydrate of the normal carbonate can exist as the solid phase. No support is furnished by this work to the suggestion that bicarbonates exist in the liquid phase. The experiments of Treadwell and Reuter,[1] and Raikow[2] where it is found that the lime (CaO) and carbonic acid (CO_2) were present in the ratio required for calcium bicarbonate, when

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[1] Zeit. anorg. Chem., 17, 170 (1898).

[2] Chem. Ztg., 28, 1247 (1904).

practically all the carbon dioxide had been removed from the gas phase, while suggestive, can not be regarded as a proof of the existence of a bicarbonate.

Magnesium Carbonates

The serious lack of agreement between the figures obtained by different investigators for the solubility of magnesium carbonate in water and in carbonated waters have been tentatively explained by the assumption of the existence of various modifications of magnesium carbonate, which pass but slowly into the stable form. Thus Wagner,[1] Beckurts[2] and Bineau[3] obtained 1.31, 8.39 and 23.3 grams magnesium carbonate per liter, respectively, in water saturated with carbon dioxide.

There is nothing to show, however, that this discordance in the earlier work was due to the presence of different solid phases. More likely, it is due to the presence of other soluble substances for Cameron and Seidell[4] have shown that the solubility of magnesium carbonate is greatly affected by the presence of other salts and recently Davis[5] has shown that pure magnesium carbonate can be prepared from its salts only with great difficulty.

It has long been known that the solubility of magnesium carbonate is greatly increased by the presence of carbon dioxide.[6]

Wagner cites a process used by Weldon for the manufacture of sodium carbonate, depending upon the fact that magnesium carbonate is more soluble in highly carbonated water than is sodium bicarbonate.

Treadwell and Reuter[7] determined the solubility of

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[1] Jour. prakt. Chem., 102, 233 (1867).

[2] Cited by Engel, Ann. Chim. Phys., (6), 13, 344 (1888).

[3] Ibid.

[4] Jour. Phys. Chem., 7, 678 (1903).

[5] Jour. Soc. Chem. Ind., 25, 788 (1906).

[6] See, for instance, Wagner: Jour. prakt. Chem., 102, 233 (1867); Engel and Ville: Compt. rend., 93, 340 (1881).

[7] Zeit. anorg. Chem., 17, 170 (1898).

magnesium carbonate in water under pressures of carbon dioxide up to one atmosphere. No attention was paid, however, to the nature of the solid phase. The authors concluded that at 14° C and with a partial pressure of carbon dioxide of zero, the solution consists of a mixture of carbonate and bicarbonate; a conclusion supported by Rinne.[1]

Davis[2] described several hydrates of magnesium carbonate and obtained solubility curves for the trihydrate and dihydrate. He found that the solid separating from a so-called solution of magnesium bicarbonate was the trihydrate of magnesium carbonate. Raikow[3] found that a solution of magnesium nitrate precipitated by a known amount of potassium hydroxide absorbed enough carbon dioxide to form the bicarbonate. Under the conditions of the experiment no solid phase remained after absorption was completed, and consequently no observations could be made upon the nature of the stable solid in equilibrium with these solutions.

The results obtained in this investigation by the action of carbon dioxide under pressure upon magnesium hydroxide in the presence of an excess of water are given in Table II. These results are brought out very clearly when plotted as in Fig. 2, the ordinates being vapor pressure and the abscissas grams of carbon dioxide added per gram of magnesium present. The curve consists of three parts. When carbon dioxide is first added there is no change in the vapor pressure until the ratio of carbon dioxide to magnesia present is that required by the formula for the normal carbonate, the point marked *A* in the diagram. On the addition of further carbon dioxide another approximately flat portion of the curve *AB* is realized, during which the solid phase appeared to diminish greatly by passing into solution, but at the point *D* the addition of further carbon dioxide appeared to produce very little effect upon the mass of solid phase in contact with the solution, while the vapor pressure increased

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[1] Chem. Ztg., 31, 125 (1907).

[2] Jour. Soc. Chem. Ind., 25, 788 (1906).

[3] Chem. Ztg., 31, 55 (1907).

TABLE II

Showing the vapor pressure of carbon dioxide over wet $Al(OH)_3$ and $Mg(OH)_2$ at 0° C. Pressures in cm. Hg

Grams CO_2 added	Pressure over $Al(OH)_3$	Grams CO_2 added	Pressure over $Mg(OH)_2$[1]
0.00	76	0.00	76
0.022	95	0.0217	76
0.036	106	0.0434	76
0.050	117	0.0651	77
0.064	130	0.0868	77
0.078	143	0.1085	77
0.092	157	0.1302	77
0.106	176	0.1519	78
0.120	193	0.1736	78.5
0.134	207	0.1953	80
0.148	223	0.2170	88
0.162	240	0.2387	88
0.176	254	0.2604	89
0.190	272	0.2821	89
0.204	289	0.3038	90
0.218	302	0.3255	112
0.232	319	0.3906	142
0.246	334	0.4557	181[2]
—	—	0.5208	242
—	—	0.5642	275

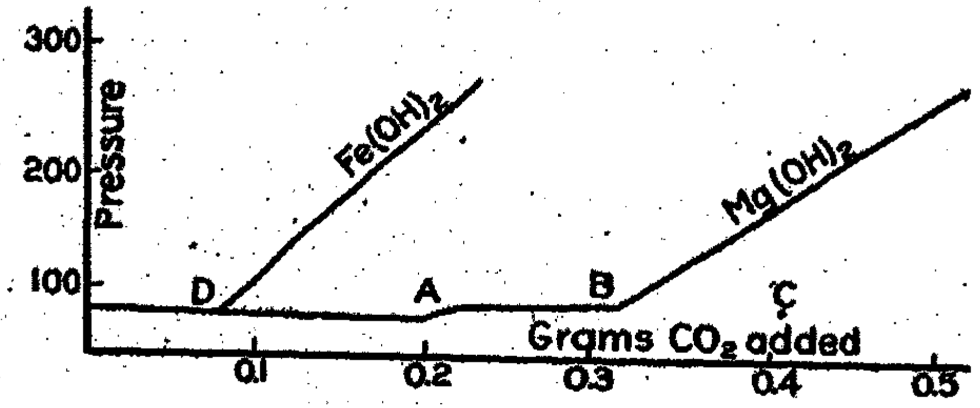

Fig. 2

practically in proportion to the further amounts of carbon dioxide added. When the absorption had been pushed as far as seemed desirable, the operation was reversed, and carbon dioxide was allowed to escape gradually in measured

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[1] Entire mass of solution 7.5 cc.

[2] Low.

quantities from the absorption chamber. It was found, however, that the vapor pressure curve thus obtained did not correspond to the one obtained by adding carbon dioxide. When the vapor pressure had fallen to the atmospheric pressure, the ratio of the amount of carbon dioxide remaining, absorbed to the magnesium oxide present, was approximately that required by the formula for magnesium bicarbonate. This experiment was repeated, although the results are not given here, since they show nothing new. The absorption curve as given, together with the hysteresis just described, was again realized. The absorption curve does not indicate the formation of any carbonate other than the normal carbonate.

Since the ratio of magnesia to carbon dioxide is that required for a bicarbonate when the excess of carbon dioxide be allowed to escape from the absorption chamber, it might be argued that the solid phase then remaining is a bicarbonate. Opposed to this, however, is the experience of previous investigators who have under very similar conditions obtained the trihydrate of the normal carbonate only. To test this point further, carbon dioxide under increased pressure was passed through a flask containing water and magnesia surrounded by ice water. It was found that the stable solid phase, was a crystalline product which persisted without noticeable change when the flask was allowed to come to room temperature. When dried by pressure between layers of absorbent paper there seemed to be a slight loss of water, but the following analytical data leaves no doubt that the substance was the trihydrate of magnesium carbonate, $MgCO_3.3H_2O$.

Theoretical: MgO, 29.16 %; CO_2, 31.79 %; H_2O, 39.05 %
Found: MgO, 29.85 %; CO_2, 31.94 %; H_2O, 38.35 %

Ferrous Carbonate

Ferrous carbonate occurs abundantly in nature as the mineral siderite. Carbonated waters have the power of dissolving this mineral and such natural solutions are known as chalybeate waters.

Hydrated ferrous carbonate[1] is precipitated by adding an alkaline carbonate solution to a ferrous salt, out of contact with air. When precipitated out of contact with oxygen, in recently boiled water, it is white. In the atmosphere it soon changes to a dirty green and ultimately to a yellowish brown hydrated ferric oxide. Raikow[2] found that freshly precipitated ferrous hydroxide absorbed slightly more carbon dioxide than would be required to form the normal carbonate.

Table I contains the analytical data realized for the pressure of carbon dioxide over wet ferrous carbonate. In Fig. 2 is plotted the curve from the data given. It will be seen that the pressure in the chamber did not rise until several charges of carbon dioxide had been forced into the chamber. Point D on the chart represents the point where all the ferrous hydroxide had been changed to the carbonate. From C to the end of the curve it is apparent that no new carbonate is formed. At the point D 0.077 grams of carbon dioxide had been forced into the chamber. There were 0.1231 grams of ferrous oxide (FeO) present, and to form the normal carbonate 0.1260 grams ferrous oxide would be required. Hence the normal carbonate and not the bicarbonate was formed under these conditions.

Ferric Hydroxide and Carbon Dioxide

It does not appear that a ferric carbonate exists. According to Gmelin[3] the precipitate obtained by adding an alkaline carbonate to a solution of ferric nitrate does not contain a trace of carbon dioxide. But Soubeiran[4] states that a precipitate obtained by adding an alkaline carbonate to solutions of ferrous salts contains 8.3 percent carbon

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[1] Watts, Dictionary of Chemistry, Vol. 1, 783 (1879).

[2] Chem. Ztg., 31, 87 (1907).

[3] Handbook, Vol. 5, 222.

[4] Ann. Chim. Phys. (2), 44, 326 (1830).

dioxide after the iron has all been oxidized by the atmosphere, Raikow,[1] however, obtained no absorption of carbon dioxide and his experiments furnish apparently conclusive evidence as to the non-existence of a ferric carbonate. The results obtained in the present investigation are given in Table I. When plotted these results all fall on a straight line, and show practically no absorption by the solid phase.

Aluminum Hydroxide and Carbon Dioxide

It is commonly stated that there is no carbonate of aluminum, although precipitates obtained by adding an alkaline carbonate to a solution of an aluminum salt contain generally small amounts of carbon dioxide. H. Rose[2] found that the aluminum hydroxide thus precipitated contained an amount of carbon dioxide, not removable by washing, corresponding to the amount of carbon dioxide held by the alkali which remained in the precipitate. Raikow[3] found that freshly precipitated aluminum hydroxide does not absorb carbon dioxide.

The results given in Table II confirm this conclusion.

Beryllium Hydroxide and Carbon Dioxide

Many basic carbonates of beryllium are described in the literature. Their large number and the extreme complexity of the formulas throws doubt on their chemical identity. Raikow[4] found that freshly precipitated beryllium hydroxide absorbed enough carbon dioxide to form a compound with the formula $BeCO_3,3Be(OH)_2$. The results given in Table I when plotted give a curve approximating quite closely a straight line. This curve though indicating a slight absorption of carbon dioxide by wet beryllium hydrate, shows conclusively that no definite carbonate is found.

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[1] Chem. Ztg., 31, 87 (1907).
[2] Pogg. Ann., 91, 452 (1854).
[3] Chem. Ztg., 31, 87 (1907).
[4] Ibid.

Conclusions

In general, it may be said that the only authentic solid bicarbonates are those of the first group of the elements, with the exception of lithium. The works of Treadwell and Reuter, and Raikow on calcium and magnesium carbonates deal only with the solution. Raikow's work on the carbonates of metals whose hydroxides are insoluble, is to be criticized on the grounds that the conditions under which he worked were most favorable to the production of solid solutions, and the presence of foreign salts in the solution may have greatly affected the character of the precipitate.

It has been shown that definite carbonates of aluminum, ferric iron, and beryllium do not exist; that bicarbonates of calcium, ferrous iron and magnesium are not formed under pressures up to five atmospheres at 0° C. While there is some evidence which supports the view that calcium bicarbonate exists in the dissolved state, the observed facts can be regarded just as logically and more conveniently as the result of the specific solvent power of the carbon dioxide-water mixture.[1]

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[1] See a recent discussion by Parsons: Jour. Phys. Chem., 11, 659 (1907).

ACTINIC ELECTROLYSIS

BY CARL GEORGE SCHLUEDERBERG

Action of Ferric Sulphate on Copper in Darkness and in Light

The following series of experiments were carried out for the purpose of determining whether any difference exists in the rates of action of ferric sulphate on copper in darkness and in light.

For this purpose pure copper was made up into a shape similar to an ordinary rotating platinum anode. Several of these copper test pieces were prepared, each of about 20 grams weight. In each experiment 300 cc of a solution of ferric sulphate of known strength was used; the copper test piece was suspended to a certain depth of solution and rotated by means of a small electric motor.

An ordinary photographic dark room was used for one set of experiments and October-November sunlight for the other set.

Most of the experiments were carried out at room temperature and in order that parallel experiments should be conducted at the same temperature, it was usually necessary to carry out the "Sunlight" experiments with the beaker of ferric sulphate solution immersed in a larger beaker of water to which ice could be added when necessary.

The following factors entered into these experiments:

(1) Time.
(2) Concentration of solution.
(3) Temperature of solution.
(4) Speed of rotation of metal test piece.
(5) Surface of metal.
(6) Volume of solution.
(7) Illumination.

The factors No. 1 and No. 2 were varied at will, and in a few instances, factor No. 3. Factors No. 4, No. 5 and No. 6 were kept as constant as possible. In the case of factor No. 7 the experiments were mostly carried out in pairs under identical conditions except that one was in total darkness and the other in the brightest obtainable sunlight.

Experiments No. 1 and No. 2

Fifty grams of ferric sulphate in 300 cc of water.
Time = 460 minutes.
Temperature = 30°.
Copper dissolved in light = 5.0459 grams.
Copper dissolved in darkness = 6.0749 grams.
Difference[1] = — 1.0290 grams.

Owing to the large amount of copper dissolved in the above experiment, amounting to about 25 percent of the total weight of the test piece, it was decided to cut down the time and the concentration.

Experiments No. 3 and No. 4

Thirty grams of ferric sulphate in 300 cc of water.
Time = 330 minutes.
Temperature = 30°.
Copper dissolved in light = 3.1270 grams.
Copper dissolved in darkness = 3.1516 grams.
Difference = — 0.0246 gram.

As the amount of copper dissolved was still too large the time and concentration were again reduced.

Experiments No. 5 and No. 6

Ten grams of ferric sulphate in 300 cc of water.
Time = 190 minutes.
Temperature = 30°.
Copper dissolved in light = 0.9981 gram.
Copper dissolved in darkness = 1.0263 grams.
Difference = — 0.0282 gram.

These experiments were immediately (same day) repeated at the temperature of melting ice with the following results:

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[1] The *difference* is marked + when the copper dissolved in light exceeds that in darkness, and — when the amount dissolved in darkness exceeds that dissolved in light.

Experiments No. 7 and No. 8

Ten grams of ferric sulphate in 300 cc of water.
Time = 190 minutes.
Temperature = Melting Ice.
Copper dissolved in light = 0.9828 gram.
Copper dissolved in darkness = 0.9483 gram.
Difference = + 0.0345 gram.

From the above results it is seen that the difference in temperature of 30° makes practically no difference in the amount of copper dissolved. Also the reaction in light is not appreciably different from that in darkness.

In the following pair of experiments the time was kept the same as before and the concentration of the ferric sulphate solution reduced to one-quarter that of the experiments immediately preceding. It is worthy of note that the copper dissolved is about one-fourth that of the preceding experiments, No. 5, No. 6, No. 7 and No. 8.

Experiments No. 9 and No. 10

2.5 grams of ferric sulphate in 300 cc of water.
Time = 190 minutes.
Temperature = 25°.
Copper dissolved in light = 0.2651 gram.
Copper dissolved in darkness = 0.2610 gram.
Difference = + 0.0041 gram.

From this pair of experiments it would seem that the reaction went at the same rate in light as in darkness, yet the possibility still existed that the reaction had been allowed to run too far toward completion for any difference to be detected in the rate, or in other words, the time allowed was too great; hence, in the following experiments, the time was shortened considerably.

Experiments No. 11 and No. 12

Ten grams of ferric sulphate in 300 cc of water.
Time, = 60 minutes.
Temperature = 25°.
Copper dissolved in light = 0.7384 gram.
Copper dissolved in darkness = 0.5347 gram.
Difference = + 0.2037 gram.

Apparently the reaction goes faster in the light, but the succeeding experiments show that this is not the case. The above difference is due to accidental variation in the speed of rotation of the metal.

Experiments No. 13 and No. 14

Ten grams of ferric sulphate in 300 cc of water.
Time = 40 minutes.
Temperature = 25°.

Copper dissolved in light	=	0.6232 gram.
Copper dissolved in darkness	=	0.6356 gram.
Difference	=	— 0.0124 gram.

Experiment 15

To test effect of speed, the same copper test piece as used in Experiment No. 14 was again rotated in darkness at a slightly lower speed under identical conditions with a loss in weight of only 0.5844 gram as against 0.6356 gram in Experiment No. 14, or a difference of 0.0512 gram of copper dissolved. Experiments No. 13 and No. 14 show practically no difference in the rate of the reaction in light and in darkness.

The differences in amounts of copper dissolved in light and darkness in Experiments No. 1, No. 2, No. 11 and No. 12 were due to accidental variation in speed of rotation. When the speed of rotation was the same in parallel experiments, practically no difference in amounts of metal dissolved in light or darkness could be detected.

Experiments No. 18 and No. 19

Ten grams of ferric sulphate in 300 cc of water.
Time = 60 minutes.
Temperature = 25°.

Copper dissolved in light	=	0.9263 gram.
Copper dissolved in darkness	=	0.9666 gram.
Difference	=	— 0.0403 gram.

In the next experiment the above time was cut in half.

Experiments No. 20 and No. 21

Ten grams of ferric sulphate in 300 cc of water.
Time = 30 minutes.
Temperature = 25°.
Copper dissolved in light = 0.6950 gram.
Copper dissolved in darkness = 0.6938 gram.
Difference = + 0.0012 gram.

This shows practically no difference in the rate in light and in darkness.

In the succeeding pair of experiments the concentration of solution was reduced to one-quarter that of the experiments immediately preceding and the time kept the same as in these experiments.

Experiments No. 22 and No. 23

2.5 grams of ferric sulphate in 300 cc of water.
Time = 30 minutes.
Temperature = 25°.
Copper dissolved in light = 0.1931 gram.
Copper dissolved in darkness = 0.1814 gram.
Difference = + 0.0117 gram.

In Experiments No. 24 and No. 25 the concentration of solution used in above experiments was cut in half.

Experiments No. 24 and No. 25

1.25 grams of ferric sulphate in 300 cc of water.
Time = 30 minutes.
Temperature = 25°.
Copper dissolved in light = 0.0923 gram.
Copper dissolved in darkness = 0.0910 gram.
Difference = + 0.0013 gram.

The above concentration of solution of ferric solution was cut in half.

Experiments No. 26 and No. 27

0.625 gram of ferric sulphate in 300 cc of water.
Time = 30 minutes.
Temperature = 25°.
Copper dissolved in light = 0.0488 gram.
Copper dissolved in darkness = 0.0458 gram.
Difference = + 0.0030 gram.

Experiments No. 28 and No. 29

1.25 grams of ferric sulphate in 300 cc of water.
Time = 30 minutes.
Temperature = 25°.
Copper dissolved in light = 0.0972 gram.
Copper dissolved in darkness = 0.1004 gram.
Difference = — 0.0032 gram.

The slight differences noticed in the four preceding pairs of experiments do not show any consistent variation in favor of light or darkness, nor are they of sufficient magnitude to indicate any such variation.

Considering the shortness of the run, the small amounts of copper dissolved and the impossibility of having the speed of the motor *exactly* the same under all conditions, the agreements are quite close.

Several experiments were carried out in which there was no stirring.

Experiments No. 30 and No. 31

2.5 grams of ferric sulphate in 300 cc of water.
Time = 190 minutes.
Temperature = 25°.
Copper dissolved in light = 0.0643 gram.
Copper dissolved in darkness = 0.0215 gram.
Difference = + 0.0428 gram.

This difference in the weight of copper dissolved is probably due to the natural circulation of the liquid in strong sunlight, for although the beaker was immersed in a larger beaker of ice water, it was impossible to keep all parts of the liquid at the same temperature for the sun shining down on the top layer of liquid would cause differences of temperature which would in turn induce some circulation of the liquid.

A fact worthy of particular note is the small amount of copper dissolved when there is no stirring. The test piece used in this case is exactly the same as that used in experiments where stirring took place.

Comparing with Experiments No. 9 and No. 10 in which the time and concentration of solution were the same as in this case, it is seen that 0.2610 gram of copper was dissolved as against 0.0215 gram without the stirring. A difference of 1200 percent in favor of stirring.

Again in Experiments No. 22 and No. 23 with concentration of solution the same as above and time reduced to thirty minutes, or one-sixth of the above, the amount of copper dissolved with stirring exceeded that dissolved without stirring by 800 percent.

As a further test of the rate of solution of copper without stirring, two strips of copper identical in size were prepared and each placed on the bottom of a large beaker and covered with a moderate amount of solution. One beaker was placed in darkness and the other beaker immersed in a larger beaker of cold water and placed in moderate sunlight, the top of the beaker being carefully covered with a block of wood and light admitted through the sides only. In this way the temperature could be kept more nearly constant throughout the solution and diffusion largely prevented.

The weight of copper dissolved in each case was more nearly the same than in the preceding experiment, though evidently some diffusion did occur in the light.

Experiments No. 33 and No. 34

1.25 grams of ferric sulphate in 150 cc of water.
Time = 230 minutes.
Temperature = 25°.

Copper dissolved in light	=	0.0628 gram.
Copper dissolved in darkness	=	0.0567 gram.
Difference	=	+ 0.0061 gram.

The reaction between copper and ferric sulphate may be expressed by the following equation: $Cu + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4$.

The preceding experiments show that this reaction proceeds at the same rate in sunlight as in darkness, and they do not give any indication that the reaction is a photochemical one.

Noyes and Whitney[1] studied the rates of solution of solid substances in their own solutions. They say "the law govern-

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[1] Noyes and Whitney: Jour. Am. Chem. Soc., 19, 930 (1897).

ing the rate of solution can be predicted with a considerable degree of probability; for the phenomenon may be considered as simply a process of diffusion. That is, we can imagine the sticks of solid substances surrounded by an indefinitely thin film of saturated solution, from which diffusion takes place into all portions of the solvent, this being kept homogeneous by rotation. If this were the case, the velocity of solution, in accordance with the law of diffusion, would be proportional to the difference between the concentration of the saturated solution and that of the solution present at the moment in question." They express the law as follows: "The rate at which a solid substance dissolves in its own solution is proportional to the difference between the concentration of that solution and the concentration of the saturated solution."

The question was further studied by Nernst[1] in an article entitled "Theory of Reaction Velocity in Non-Homogeneous Systems." In this article he takes the view that at the common surface of two phases equilibrium is established with great rapidity, and that the rate actually measured is that of diffusion throughout the liquid phase.

Thus, the principle, enunciated by Noyes and Whitney in connection with a physical change, is here applied to chemical and electrochemical reactions.

The case of the solution of magnesia in acids is cited, and it is assumed that the solution in immediate contact with the magnesia is saturated with the substance, and therefore slightly alkaline. Therefore, the rate of the reaction is simply that at which the acid diffuses to the common surface; if the acid is thoroughly stirred, the fall of concentration will be confined to a very thin layer surrounding the solid magnesia. For given conditions, this rate is constant and may be determined.

The same reasoning is applied to electrochemical cases where the common surface is that of the electrode. By

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[1] Nernst: Zeit. phys. Chem., 47, 52 (1904).

keeping down the concentration the same formula may be applied as in purely chemical cases.

Erich Brunner[1] in an article entitled "Velocity of Reaction in Non-Homogeneous Systems" describes some experimental investigations of these theories. He derives a formula for the rate of solution of benzoic acid in water, which for a given rate of stirring and of temperature, involves the volume and the concentration of a saturated solution and successive values of the concentration of the dilute solution at a known interval of time. The rate of solution is found to bear a certain relation to the speed at which the stirring apparatus is revolved.

The velocity of reaction should be independent of the nature of the solid substance, provided that the concentration of the diffusing substance is practically zero at the surface of the solid.

In harmony with this it is found that the rates of solution of basic magnesium carbonate, magnesium hydroxide, and magnesium itself in benzoic acid are approximately equal. Magnesium and magnesium hydroxide dissolve equally rapidly in hydrochloric acid.

The velocity of electrolytic separation of hydrogen at a platinized platinum electrode from solutions of benzoic and hydrochloric acids containing an excess of potassium chloride, is, within certain limits, equal to the rate of solution of magnesium hydroxide.

Other reactions are studied which agree very well with the theory. A comparison of the rates of solution of magnesium hydroxide in different acids in the presence of their magnesium salts shows that they increase in the following series, benzoic, acetic, formic, hydrochloric, which order is the same as if these acids were arranged according to the magnitude of their diffusion coefficients.

My experiments, although they gave a negative result so far as any photochemical action is concerned, nevertheless

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[1] Brunner: Zeit. phys. Chem., 47, 56 (1904).

furnish a striking example of the theory that the rates of many reactions are simply rates of diffusion and not rates of chemical reactions.

The reaction between copper and ferric sulphate is practically instantaneous and the observed rate depends entirely on the speed with which stirring is carried on. For instance, it is seen on comparing Experiments No. 9 and No. 10, which were carried out with stirring, with Experiments No. 30 and No. 31 in which the conditions were identical except for stirring, that about twelve times as much copper dissolved when there was an opportunity for diffusion of the copper sulphate and ferrous sulphate away from the surface of the copper, as in the case where no stirring occurred and the diffusion was consequently slower, especially in consideration of the fact that the absence of light would tend to prevent any natural diffusion. We know that, in the case of the electrolytic deposition of metals, the rate is only limited by the speed of rotation of the cathode.

In the same way it may be said that the rate of solution of a metal or substance is only limited by the mechanical possibility or difficulties of rotation of the specimen of metal or substance or of the stirring of the solution.

Thus, these results show that the reaction between copper and ferric sulphate is practically instantaneous and that, if there is anything of a photochemical nature above it, ordinary means of measurement will not detect it. They agree with and tend to confirm the work of Noyes and Whitney, Nernst and Brunner, already cited.

Electrolytic Chlorination of Acetic Acid, Benzene and Toluene

In the following sets of experiments the attempt is made to study the chlorination of several organic substances by electrolytic means and under varying conditions.

ACETIC ACID

Experiment 1.—Twenty grams of zinc chloride were dissolved in 300 cc of glacial acetic acid and electrolyzed in the dark at 20° with platinum electrodes, the cathode being enclosed in parchment diaphragm electrodes, 11 × 1.5 cm.

It being impossible to get any current through the liquid at 100 volts pressure, water was gradually added up to about 25 cc. Current went to one-half ampere plus, and voltage dropped to 25 volts.

The solution became hot and some zinc, which had been deposited on the outside of the parchment diaphragm, was redissolved slowly by the liquid.

After one and one-quarter hours the current was shut off and 10 cc of the solution removed for analysis, as it was desired to determine the amount of halogen substituted in the acetic acid.

To get rid of any dissolved chlorides present in the portion pipetted off, silver nitrate was added in excess and the precipitated silver chloride was removed by filtration. Free chlorides having been thus removed, the filtrate was then boiled for some time in a flask with return condenser, thus hydrolyzing any chlor acetic acid which might be present and precipitating the chlorine as silver chloride which was collected on a Gooch filter and weighed in the usual manner.

Total silver chloride in 300 cc. liquid = 0.09 gram.
Chlorine in 0.09 gram silver chloride = 0.0223 gram.
1.25 hours × 0.5 amperes = 0.625 amp. hrs.
0.625 ampere hours are equivalent to = 0.825 gram Cl.
Chlorine available for substitution = 0.412 gram.

$$\text{Efficiency} = \frac{0.0223}{0.412} \times 100 = 5.42 \text{ percent.}$$

Experiment 2.—200 grams of acetic acid, excess zinc chloride. Porous cup. Cathode same size as in Experiment 1 placed in cup. Anode about three times as large as in Experiment 1. Temperature = 0°. Electrolysis in the dark. Voltage 25 at first, rapidly fell to 7 volts. Analysis same as before.

Total silver chloride in 200 cc = 0.2340 gram.
Chlorine in 0.2340 gram AgCl = 0.0578 gram.
Five hours × 0.25 ampere = 1.25 amp. hrs
1.25 ampere hours equivalent to = 1.65 grams Cl.
Chlorine available = 0.82 gram.
Efficiency = 7.05 percent.

From this experiment it is seen that lowering the anode current density and diminishing the temperature of the solution has resulted in but a very slight increase in efficiency.

Experiment 3.—Same as Experiment 2, except that a platinum wire was used for anode in order to try effect of increase in current density at anode.

Voltage 110 **Analyzed 10 cc portion**
Total silver chloride in 200 cc = 0.4480 gram.
Chlorine in 0.448 gram AgCl = 0.1110 gram.
Fifteen hours × 0.2 amperes = 3.00 amp. hrs.
3.00 ampere hours equivalent to = 3.96 grams Cl.
Chlorine available = 1.98 grams.
Efficiency = 5.6 percent.

Using wire anode and consequently high current density did not give a better yield of substituted acetic acid.

Experiment 4.—A repetition of Experiment 2 gave equally unsatisfactory results, although the time of the electrolysis was extended over about 20 hours. Efficiency about 1 percent.

Due to the poor conductivity of acetic acid, even with zinc chloride dissolved in it, a high voltage across the terminals of the cell was necessary in order to force an appreciable current through the electrolyte. On account of the consequently large potential gradient in the electrolyte, metallic zinc was usually deposited on the surface of the diaphragm surrounding the cathode. (Electrostenolysis).

As this zinc gradually dissolved, giving off bubbles of gas, it would seem that it reacted with a larger part of the chlor acetic acid formed, reducing same with the formation of zinc chloride and the evolution of hydrogen.

Possibly this accounts for the poor yield of substituted acetic acid, especially in Experiment 3 where the time was lengthened out to twenty hours, thus giving ample opportunity for the deposited zinc to react on the solution. If the above explanation is correct obviously no matter how the time of the run might be extended, the results would be equally unsatisfactory.

As a test experiment, metallic zinc was treated with mono-chlor acetic acid. The metal dissolved slowly and the resulting solution gave a precipitate with silver nitrate, thereby showing the formation of zinc chloride and the destruction of the chlor acetic acid.

Experiment 5.—In order to overcome trouble caused by the precipitated zinc reducing the chlor acetic acid dry hydrogen chloride was passed into glacial acetic acid for one hour. A portion of the acid on addition of silver nitrate gave precipitate of silver chloride, showing the absorption of some of the hydrogen chloride by the acetic acid. This was electrolyzed for five hours under conditions similar to Experiment 4. Voltage 110, current 0.2 ampere at start gradually fell to below 0.1 ampere. On analysis only a trace of substituted acid was obtained.

Evidently the amount of hydrogen chloride absorbed was very small and hence the lack of satisfactory results.

Experiment 6.—In this experiment use was made of an H tube in order to protect the chlor acetic acid from being acted on by the zinc by confining it to one arm of the H and the zinc to the other. The wire anode was placed in one arm of the H and the platinum strip cathode in the other arm. The two arms of the H were of course closed at the lower ends. In this was placed 80 cc of acetic acid saturated with zinc chloride.

Temperature = 20°,—Diffused light.

Weight AgCl in 10 cc = 0.0350 gram.
Total AgCl in 80 cc = 0.2800 gram.
Chlorine in 0.2800 gram AgCl = 0.0693 gram.
Twenty-seven hours × 30 milliamperes = 0.810 amp. hrs.
0.810 amp. hrs. equivalent to = 1.07 grams Cl.
Chlorine available = 0.535 gram.
Efficiency = 12.9 percent.

Evidently from the higher efficiency obtained, this procedure partially overcomes the reduction of the chlor acetic acid by the precipitated zinc, as free circulation of the electrolyte is prevented, and by having the cathode arm of the H shorter than the other arm, a large part of the acid does not come into contact with the cathode. However, the efficiency is still very low, making the electrolytic chlorination unsatisfactory.

Experiment 7.—One hundred cc of glacial acetic acid was mixed with 10 cc of concentrated hydrochloric acid and electrolyzed at room temperature—20°—in very diffused light. Voltage 15.

Ten cc taken for analysis.
Weight of silver chloride obtained = 0.0220 gram.
Total silver chloride in 110 cc = 0.2420 gram.
Chlorine in 0.242 gram AgCl = 0.0600 gram.
Ten hours — 0.2 ampere = 2 amp. hrs.
Two ampere hours equivalent to = 2.64 grams Cl.
Chlorine available = 1.32 grams.
Efficiency = 4.55 percent.

Hydrochloric acid, as a source of chlorine, does not give any better efficiency than obtained in the previous experiments with zinc chloride. Anhydrous hydrochloric acid, were it sufficiently soluble in acetic acid, would probably work much better than the ordinary concentrated acid which, of course, introduces considerable water.

Experiment 8.—Two hundred cc of glacial acetic acid was placed in a liter bottle in which was 3.4 grams of platinum black and platinum foil. Room temperature = 20°. Acid was saturated with chlorine and bottle filled with same, then stoppered and placed in a dark cupboard.

Started, December 10, 1906.
Finished, May 13, 1908.
Elapsed time, 5 months.
Analysis of 10 cc portion gave:

Weight of silver chloride = 0.0123 gram.
Total silver chloride in 200 cc = 0.2460 gram.
Total chlorine = 9.0610 gram.
Corresponds to 0.1625 gram of $CH_2ClCOOH$.

The amount of substitution taking place under these conditions is very small indeed, especially when the fact that the experiment extended over 5 months time is taken into consideration.

From the foregoing series of experiments it is evident that, while it is possible to chlorinate acetic acid electrolytically, yet from the standpoint of efficiency, the results obtained are of a very unsatisfactory nature.

In the first place, glacial acetic acid, even when saturated with zinc chloride, is such a poor conductor as to make it impossible to get an appreciable current through it with 110 volts pressure.

With ordinary acetic acid an appreciable current can be gotten through at this voltage, but the potential gradient is very high and metallic zinc is deposited on the diaphragm, which causes decomposition of the chlor acetic acid and cuts down the yield; but even when this trouble is eliminated the efficiency is still loo low.

Neither variations in temperature from that of melting ice to ordinary room temperature, nor variations in the anode current density seem to make an appreciable difference in the efficiency.

In the beginning of this work it was postulated (1) that light causes a dissociation, (2) dissociation effects of light can be duplicated electrolytically, (3) when light and halogen carriers act in the same way, the results can be duplicated electrolytically.

The ordinary chemical chlorination of compounds of the type of acetic acid is best carried out in sunlight, and in the presence of certain carriers, such as phosphorus.

It was thought that the chlorine obtained electrolytically, and ordinary chlorine, in the presence of sunlight, would act in the same manner; but it has since been found in the chlorination of toluene that these two kinds of chlorine act differently. In toluene, electrolytic chlorine substituted in the ring, and ordinary chlorine, in the presence of sunlight, in the side chain. Thus, it would seem that the hydrogen in acetic acid, which is substituted by chlorine in the sunlight, is of the same kind as that in the side chain of toluene. This chlorine is designated as positive in distinction to the ring chlorine of toluene or benzene which is called negative.

It has been assumed that light causes a dissociation of chlorine into positive and negative chlorine.[1]

When acetic acid is chlorinated in sunlight the positive chlorine can be considered as displacing the hydrogen of the acid, which subsequently unites with the remaining negative chlorine to form hydrogen chloride.

Postulate No. 2 that the dissociation effects of light can be duplicated electrolytically, therefore does not hold.

Postulate No. 3, as it reads, does not hold, but then only a few carriers act in the same way as light, among them phosphorus. When a carrier acts in a different sense from light, its action can be duplicated electrolytically.

An ordinary carrier, such as ferric chloride, can be considered as dissociating into ferrous chloride and negative chlorine. The action of such a carrier can be duplicated electrolytically. With phosphorus pentachloride, dissociation may occur into phosphorus trichloride and positive chlorine, thus acting in the same sense as light.

Since in all cases in the electrolytic chlorination of acetic acid the efficiency obtained was extremely low, it is safe to assume that what chlorination did occur, was due to ordinary chlorine gas discharged from the electrode and dissolved in the acid, and not to the negative chlorine as set free from the anode.

Chlorination of Benzene

The electrolytic chlorination of benzene was studied under varying conditions and with several sources of chlorine.

In these first experiments, as a source of chlorine, ether was saturated with zinc chloride and then added to the benzene about to be electrolyzed. The total chlorine was determined with alcohol and excess of sodium according to the method of

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[1] Bancroft: Jour. Phys. Chem., 12, 439 (1908).

Stephanow.[1] By subtracting the free chlorides obtained by direct precipitation with silver nitrate, the substituted chlorine was obtained.

Experiment 1.—A mixture of 80 cc of benzene and 80 cc of ether saturated with zinc chloride was electrolyzed at 25° with porous cup and platinum electrodes. 110 volts, dark.

Total silver chloride = 0.7984 gram.
Total chlorine = 0.1970 gram.
Fifteen hours × 25 M. A. = 0.375 amp. hrs.
0.375 ampere hours equivalent to = 0.495 grams Cl.
Chlorine available = 0.247 gram.
Efficiency = 80.0 per cent.

Experiment 2.—Electrolyzed a mixture of 60 cc of benzene and 75 cc of ether saturated with zinc chloride. Porous cup, dark, temperature = 25°, platinum electrodes 1.5 × 12 cm, volts = 100.

Total silver chloride = 0.7260 gram.
Total chlorine = 0.180 gram.
Twenty-four hours × 15 M. A. = 0.360 amp. hrs.
0.360 amp. hrs. equivalent to = 0.475 gram Cl.
Chlorine available = 0.237 gram.
Efficiency = 76.0 percent.

Experiment 3.—The chlorination of benzene was next tried, using as a source of chlorine a solution of sodium chloride, sulphuric acid and water.[2] The advantage of this solution is that it will absorb very little chlorine.

A Classen dish and rotating anode were used, the anode being arranged so as to be entirely in the upper or benzene portion of the solution. Seventy-five cc of Oettel solution and 75 cc of benzene were used. Temperature = 0°.

Total silver chloride = 0.2600 gram.
Total chlorine = 0.0643 gram.
Two hours × 2 amperes = 4.0 amp. hrs.
4 ampere hours equivalent to = 5.28 grams Cl.
Chlorine available = 2.64 grams Cl.
Efficiency = 2.29 percent.

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[1] Stephanow: Ber. chem. Ges., Berlin, 39, 4056 (1906).

[2] Felix Oettel: Zeit. Elektrochemie, 2, 58 (1895), 160 grams NaCl, 140 grams H_2SO_4, made up to a liter with water.

Efficiency obtained with this arrangement is very low, possibly due to the temperature or to the electrolyte and high current density. As the other methods of electrolytic chlorination gave satisfactory results, the causes of the poor efficiency obtained in this experiment were not investigated further at the time.

Experiment 4.—From the preceding three experiments it is seen that chlorine when set free at the anode of an electrolytic cell will substitute in the benzene ring. In this connection the question came up as to what would be the action of chlorine on the benzene ring when obtained from another source, such as an instable chlorine compound. Lead tetrachloride was prepared and used as a source of chlorine. This compound, being of a very instable nature, beaks down on introduction into benzene, giving off two chlorine atoms and forming insoluble lead chloride.

$$PbCl_4 = PbCl_2 + Cl_2.$$

Twenty cc of cold benzene were treated with 3.5 grams of lead tetrachloride, added a drop at a time, in darkness. The odor of hydrochloric acid was noticeable and the benzene turned a beautiful red color, which, however, disappeared after about an hour's time leaving a clear solution with a white precipitate of lead chloride at the bottom of the beaker. A certain amount of white precipitate was formed, together with the red color of the solution, immediately the first drop of lead tetrachloride was added.

Total silver chloride = 0.3860 gram.
Chlorine = 0.0958 gram.
3.5 grams $PbCl_4$ equivalent to = 0.7120 gram Cl.
Chlorine available = 0.356 gram.
Efficiency = 26.9 percent.

Experiment 5.—Twenty-five cc of benzene treated with 6 grams of lead tetrachloride, cold, dark.

Total silver chloride = 1.4895 grams.
Chlorine = 0.368 gram.
Six grams $PbCl_4$ equivalent to = 0.122 gram Cl_2.
Chlorine available = 0.61 gram.
Efficiency = 60.4 percent.

From the above experiments it is seen that chlorine from an instable compound of chlorine will substitute in the benzene ring.

The larger quantity of lead tetrachloride used in Experiment 5 may account for the increase in efficiency over Experiment 4.

From the foregoing experiments it is seen that electrolytic chlorine will replace hydrogen in the benzene ring. Again, chlorine from the decomposition of lead tetrachloride replaces the hydrogen of the ring in a similar manner. It is known that when chlorine is passed into benzene in the presence of a carrier such as ferric chloride, substitution takes place. Thus, the final result is the same with electrolytic chlorine, as that from an instable chlor compound, or chlorine in the presence of a carrier such as ferric chloride.

In an article on halogen carriers Lothar Meyer[1] considered that in the chlorination of benzene in the presence of ferric chloride, an addition compound is first formed between the benzene and the ferric chloride. This compound, in the presence of free chlorine, then breaks down, whereupon the chlorine of the carrier unites with the hydrogen of the benzene forming hydrogen chloride, and each is replaced by an atom of the free chlorine. In the same way, if benzene were being brominated with ferric chloride as a carrier, hydrogen chloride would first be formed and then the free bromine would substitute in the ring and in the carrier. According to this theory, substitution in the ring takes place subsequent to the formation of hydrogen chloride.

On the basis of this theory of Lothar Meyer's, the formation of chlorobromobenzene compounds in the bromination of benzene, with ferric chloride as a carrier, would be out of the question, nor does he speak of having obtained any such compounds in the course of his work. However, an article appeared a few years later which places the subject in quite a different light.

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[1] L. Meyer: Jour. prakt. Chem., 142, 502 (1886).

MacKerrow,[1] in studying bromine carriers, used ferric chloride as a carrier in the bromination of several nitrobenzenes. In a number of cases he found that chlorine substituted along with the bromine, giving compounds such as chloropentabromobenzene, dichlorotetrabromobenzene and tetrachlorodibromobenzene.

If, however, as Meyer claims, substitution takes place subsequent to the formation of hydrogen chloride, it would be hard to account for the fact that MacKerrow found the chlorine from the ferric chloride substituted in the benzene ring instead of being evolved as hydrogen chloride.

In view of these facts, it would seem that the action of the carrier can be explained in a manner more nearly correct by assuming that the chlorine of the ferric chloride, which may be designated as negative chlorine, displaces the hydrogen of the ring, which may also be considered as negative in character, thus forming a chlor-benzene.

Subsequently, this hydrogen unites with other chlorine from ferric chloride and is evolved as hydrogen chloride or in the case of bromination, as hydrogen bromide. The carrier which has been thus deprived of part of its chlorine combines with any free halogen present, say bromine, and forms a ferric chlor bromide. This, in turn, can act as a carrier just as before, causing more halogen to substitute in the ring and it may be converted finally into ferric bromide.

When acting as a carrier, ferric chloride may be looked upon as dissociating into ferrous chloride and negative chlorine, according to the following equation

$$Fe_2Cl_6 \longrightarrow Fe_2Cl_4 \text{ and } 2Cl^-.$$

Part of the negative chlorine obtained from the ferric chloride may then displace some of the hydrogen of the benzene ring, which is also considered to be negative in character, thus forming chlorbenzene. Subsequently this hydrogen unites with the remaining negative chlorine, forming hydrogen chloride.

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[1] MacKerrow: Ber. chem. Ges., Berlin, 24, 2939 (1891).

In the presence of free chlorine, the ferrous chloride is changed to ferric chloride, in which condition it is ready to again act as a carrier.

When acting as a carrier in the bromination of benzene, a compound such as $Fe_2Cl_4Br_2$ may be formed, which in turn, may give up more chlorine to the benzene and be converted finally to ferric bromide, or what seems more probable, the hydrobromic acid split off may react with a compound such as $Fe_2Cl_4Br_2$ reducing it to ferric bromide and evolving hydrogen chloride.

This is substantiated by the fact, that ferric chloride when used as a carrier in the bromination of benzene is converted to ferric bromide.[1] This theory accounts for the formation of chlorobromobenzenes when ferric chloride is used as a carrier in the bromination of benzene, which compounds cannot be accounted for on the basis of the assumption made by Lothar Meyer.

In the same manner, it may be assumed that the negative electrolytic chlorine displaces the hydrogen of the ring and the chlorine from lead tetrachloride, which may be considered as negative, acts in the same way. The theory also accounts for the reaction velocity, in the case of ferric chloride, benzene, and chlorine, being found proportional to the first power of the concentration of the ferric chloride.[2]

MacKerrow also studied the action of ferric chloride, alone, on dinitrobenzene. He heated the mixture to a very high temperature and in one case an explosion occurred, and on a second trial a complete breakdown took place, giving some hydrogen chloride and ferrous chloride in addition to other products.

Page,[3] in studying inorganic chlorides as chlorine carriers, tried the experiment of heating ferric chloride with benzene in a sealed tube a temperature of 100°. On opening the tube there was no evidence of any gas pressure. A part of the

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[1] Meyer and Scheufelen: Liebig's Ann., 231, 164 (1885).

[2] Slator: Jour. Chem. Soc., 83, 729 (1903).

[3] Page: Liebig's Ann., 225, 205 (1884).

benzene was charred and formed a black bituminous mass with the ferric chloride. He was not able to detect ferrous salt either in the liquid or in the residue. From this he concludes that ferric chloride, when acting as a carrier, cannot, by giving up its chlorine to the ring compound, be reduced to ferrous chloride and be changed back again to ferric chloride. He then proceeds to build up a theory of addition products similar to the one cited in this paper under Lothar Meyer's work.

Now, if it could be shown that ferric chloride alone will react with benzene, considerable support would be extended to the theory that the chlorine of the carrier displaces the hydrogen of the benzene and that subsequently hydrogen chloride is formed. With this in mind the following experiments were performed.

Experiment 6.—In this experiment 65 cc of benzene were mixed with 12 grams of pure anhydrous ferric chloride in a round bottom flask fitted with a return condenser. This was exposed to bright sunlight for four hours and occasionally heated with a Bunsen burner. A brisk reaction took place, lasting considerable time after each heating, apparently evolving considerable heat, as the liquid was kept at the boiling point for some ten minutes or more in each instance. The odor of hydrochloric acid could be detected at the top of the return condenser and moist litmus paper gave test for acid. At the end of the above-mentioned time, the supernatant liquid, after being allowed to cool, was poured off. This had a decided deep brown color. With a hard filter and suction this liquid was obtained as a clear brownish yellow oil.

On analysis of a 10 cc portion, the following results were obtained:

Substitution	= 0.0425 gram AgCl.
Total silver chloride	= 0.2762 gram AgCl.
Total chlorine	= 0.0684 gram Cl.
Equivalent to	= 0.227 gram C_6H_5Cl.

The brown supernatant liquid when added to potassium ferricyanide gave a blue color (Turnbull's blue), thus indicating the presence of iron in the ferrous condition.

This experiment shows that it is possible to chlorinate benzene with a chlorine carrier, "ferric chloride," in the absence of free chlorine, provided the experiment be carried out in the sunlight and at a sufficiently high temperature to start the reaction and cause it to proceed at a fairly rapid rate, but not so hot as to cause a breakdown.

The lack of success of Page and other experimenters in this line is probably accounted for by the fact that they failed to carry out the experiment in sunlight and also heated to too high a temperature.

Thus it is seen that electrolytic chlorine which may be considered as negative; chlorine from an instable compound, such as lead tetrachloride, which may also be considered as negative, and chlorine from ferric chloride, also negative, all react with benzene in a similar and consistent manner. These facts are satisfactorily accounted for by the theory that the negative hydrogen of the benzene ring is displaced by negative chlorine and that it subsequently forms hydrogen chloride.

ADDITION PRODUCTS.

As a matter of interest the action of gaseous chlorine on benzene in the presence of dilute sodium hydroxide solution, and then in the presence of water, was studied with the object of determining the amount of addition and substitution products formed in each case.

Mathews[1] makes the statement that the formation of chlorine addition products of benzene proceeds best in the presence of a very dilute solution of sodium hydroxide and *almost* as well within the presence of water. No figures are given comparing the relative amounts of benzene hexachloride formed in the two cases, nor were any experiments made to determine whether any substitution products were

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[1] Mathews: Jour. Chem. Soc., 59, 166 (1891).

formed when the chlorination was carried out in the presence of water or any other solution, though the possibility of the formation of substitution compounds is mentioned.

The total chlorine was determined by sodium, alcohol, and precipitation as silver chloride—method of Stephanow. The addition chlorine was determined by boiling the oil with alcoholic caustic soda, precipitating the chlorine as silver chloride and multiplying the result by 2 as in this method only half the chlorine is split off.

$$C_6H_6Cl_6 = C_6H_3Cl_3 + 3HCl.$$

Experiment 7.—In an ordinary gas wash bottle were placed 100 cc of benzene and 75 cc of a 1 percent solution of sodium hydroxide. This was placed in very diffused light and at room temperature—20°—chlorine gas bubbled in at a fairly rapid rate for one and one-half hours. The gas passed first into the hydroxide solution and from there to the upper layer of benzene where it was absorbed. The benzene took on a yellow color and in some cases a portion of it fell to the bottom of the bottle due to the increase of specific gravity consequent to the absorption of chlorine. During the passage of chlorine into the benzene an increase of temperature was noticed.

Before analysis the benzene was washed repeatedly in a separatory funnel to eliminate all free chlorine.

Analysis of 5 cc portions gave

Total chlorine	2.2610 grams AgCl.
Addition chlorine	2.2680 grams AgCl.
Percent addition	100 percent.

Evidently in this case all the chlorine goes to form benzene hexachloride.

Experiment 8.—One hundred cc of benzene, 75 cc of water in gas wash bottle. Chlorine passed in for one and one-half hours, room temperature, 20°, very diffused light. Benzene turned yellow in color, same as in Experiment 6, and slight increase in temperature was noticed.

Analysis of 5 cc portions gave

Total chlorine = 2.3376 grams AgCl.
Addition chlorine = 2.2664 grams AgCl.
Difference = 0.0712 gram AgCl.
Percent addition = 96.8 percent.
Percent substitution = 3.2 percent.

The results of these experiments show that with dilute caustic solution all the chlorine goes to form addition products while when pure water was used some substituted benzene was formed as well as benzene hexachloride.

Chlorination of Toluene

A study of the chlorination of toluene under varying conditions was next taken up.

Experiment 1.—In a Classen dish with rotary platinum anode were placed 100 cc of toluene and 175 cc of an Oettel solution. Very diffused light, temperature of melting ice.

Total silver chloride = 1.3070 grams.
Side chain silver chloride = 0.3125 gram.
Ring silver chloride, difference = 0.9945 gram.
Total chlorine = 0.3235 gram.
Six hours × 2 amperes = 12.0 amp. hrs.
12 ampere hours equivalent to = 15.86 grams Cl.
Chlorine available = 7.93 grams.
Efficiency = 4.07 percent.
Percentage ring = 76.1 percent.
Percentage chain = 23.9 percent.

Experiment 2.—Same as Experiment 1, except that the time of the electrolysis was reduced to five hours instead of six hours and the experiment was carried out in total darkness.

Total silver chloride = 1.8225 grams.
Side chain silver chloride = 0.4270 gram.
Ring silver chloride = 1.3955 grams.
Total chlorine = 0.4510 gram.
Five hours × 2 amperes = 10.0 amp. hrs.
10 ampere hours equivalent to = 13.22 grams Cl.
Chlorine available = 6.61 grams.
Efficiency = 6.82 percent.
Percentage ring = 76.6 percent.
Percentage chain = 23.4 percent.

It is worthy of note that these two experiments check each other quite well as regards the percentage of chlorine in side chain and in ring. The slight difference in efficiency may be due to the anode being farther from the lower layer of Oettel solution and more exposed to the toluene.

Chlorination of Toluene at Low Current Density

Experiment 3.—Seventy-five cc of toluene and 100 cc Oettel solution in Classen dish, rotating platinum anode, temperature melting ice, very diffused light.

Total silver chloride = 1.3764 grams.
Side chain silver chloride = 0.0552 gram.
Ring silver chloride = 1.3212 grams.
Total chlorine = 0.3405 gram.
Fifteen hours × 0.09 ampere = 1.35 amp. hrs.
1.35 amp. hours equivalent to = 1.78 grams Cl.
Chlorine available = 0.89 gram.
Efficiency = 38.25 percent.
Percentage ring = 95.98 percent.
Percentage chain = 4.02 percent.

From the results obtained in this experiment it would seem that, by lowering the current density, the percentage substitution in the ring is increased and that of the side chain reduced to a very small figure. Also, the total efficiency is much higher than before.

Electrolytic Chlorination of Boiling Toluene

Experiment 4.—For this experiment a wide-mouth pear-shaped flask was fitted with a return condenser and platinum electrode, the cathode being a strip of platinum, 1.5 x 12 cm., doubled on itself and covering the bottom of the flask. The anode was of the regulation rotating type. During the course of a run the cathode was completely immersed in the lower liquid layer which was the source of chlorine. The cathode was connected to a short platinum wire sealed into a bent glass tube which extended from the bottom of the flask through the cork. The shank of the anode was sealed into a glass tube passing through the cork in such a manner that by sliding same up or down, or by twisting, the position of the anode could be adjusted as desired. The flask was rested on a sand bath and heated by a Bunsen burner.

One hundred cc toluene, 175 cc Oettel solution, diffused light, boiling temperature, anode in toluene:

Total silver chloride = 21.4500 grams.
Side chain silver chloride = 9.6105 grams.
Total chlorine = 5.3200 grams.
Six hours × 2 amperes = 12.0 amp. hrs.
Twelve ampere hours equivalent to = 15.86 grams Cl.
Chlorine available = 7.93 grams.
Efficiency = 66.9 percent.
Percentage ring = 55.3 percent.
Percentage chain = 44.7 percent.

Experiment 5.—In this experiment three electric light carbons bunched together were used for anodes and platinum for cathode.

Seventy-five cc of toluene and 175 cc of Oettel solution were electrolyzed at boiling temperature in very diffused light.

Total silver chloride = 2.4757 grams.
Side chain silver chloride = 0.7035 gram.
Ring silver chloride = 1.7722 grams.
Total chlorine = 0.6140 gram.
Six hours × 2 amperes = 12.0 amp. hrs.
12 ampere hours equivalent to = 15.86 grams Cl.
Chlorine available = 7.93 grams.
Efficiency = 7.73 percent.
Percentage ring = 71.55 percent.
Percentage chain = 28.45 percent.

Experiment 6.—This experiment is identical with Experiment 5, except that it was carried out in absolute darkness.

Total silver chloride = 1.9987 grams.
Side chain silver chloride = 0.450 gram.
Ring silver chloride = 1.5487 grams.
Total chlorine = 0.495 gram.
Six hours × 2 amperes = 12.0 amp. hrs.
Twelve ampere hours equivalent to = 15.86 grams Cl.
Chlorine available = 7.93 grams.
Efficiency = 6.22 percent.
Percentage chain = 22.6 percent.

In this and the experiment preceding, the carbon anode suffered considerable disintegration, the entire solution being filled with powdered carbon and the bottom of the flask was covered with a layer of it. The chlorine at the anode may have attacked the binding material of the carbon instead of substituting in the toluene, thus accounting for the low efficiency in Experiments 5 and 6.

Experiment 7.—Graphite block was substituted for the gas carbon as anode.

Seventy-five cc of toluene, 175 cc of Oettel solution, diffused light:

Total silver chloride = 14.3295 grams.
Side chain silver chloride = 6.0367 grams.
Ring silver chloride = 8.2928 grams.
Total chlorine = 3.54 grams.
Six hours × 2 amperes = 12.0 amp. hrs.
Twelve ampere hours equivalent to = 15.86 grams Cl.
Chlorine available = 7.93 grams.
Efficiency = 44.50 percent.
Percentage ring = 57.8 percent.
Percentage chain = 42.2 percent.

Experiment 8.—The above experiment was repeated with conditions identical except that all light was excluded.

Total silver chloride = 12.0885 grams.
Side chain silver chloride = 5.0767 grams.
Ring silver chloride = 7.0118 grams.
Total chlorine = 2.995 grams.
Six hours × 2 amperes = 12 amp. hrs.
Twelve ampere hours equivalent to = 15.86 grams Cl.
Chlorine available = 7.93 grams.
Efficiency = 37.7 percent.
Percentage ring = 58.2 percent.
Percentage chain = 41.8 percent.

From the above results it is seen that there is very little difference between *darkness* and *very diffused light*, at least so far as the percentage ring and chain substitution is concerned. What difference there is, is in the right direction, for a higher percentage of side chain chlorine is expected in the light than in darkness from the results obtained in the ordinary chlorination of boiling toluene in sunlight.

Experiment 9.—In this experiment the arrangement was the same as that used in Experiment 4, except that concentrated hydrochloric acid was substituted for the Oettel solution.

Seventy-five cc of toluene and 100 cc of concentrated hydrochloric acid, platinum anode, boiling temperature.

Total silver chloride = 7.8495 grams.
Side chain silver chloride = 1.1092 grams.
Ring silver chloride = 6.7403 grams.
Total chlorine = 1.9850 grams.
Six hours × 2 amperes = 12.0 amp. hrs.
Twelve ampere hours equivalent to = 15.86 grams Cl.
Chlorine available = 7.93 grams.
Efficiency = 25.00 percent.
Percentage ring = 85.85 percent.
Percentage chain = 14.15 percent.

In this experiment the platinum anode was dissolved and after four hours a gas carbon electrode was substituted. This electrode was disintegrated to some extent.

Experiment 10.—In this and the next experiment the conditions were identical with Experiments 7 and 8, except that concentrated hydrochloric acid was substituted for the Oettel solution.

Seventy-five cc of toluene, 100 cc of concentrated hydrochloric acid, diffused light, boiling toluene, graphite anode.

Total silver chloride = 16.2097 grams.
Side chain silver chloride = 5.7000 grams.
Ring silver chloride = 10.5097 grams.
Total chlorine = 4.02 grams.
Six hours × 2 amperes = 12.0 amp. hrs.
Twelve ampere hours equivalent to = 15.86 grams Cl.
Chlorine available = 7.93 grams.
Efficiency = 50.5 percent.
Percentage ring = 64.8 percent.
Percentage chain = 35.2 percent.

Experiment 11.—This is identical with the above experiment except that all light was excluded.

Total silver chloride = 22.4512 grams.
Side chain silver chloride = 6.7177 grams.
Ring silver chloride = 15.7335 grams.
Total chlorine = 5.57 grams.
Six hours × 2 amperes = 12.0 amp. hrs.
Twelve ampere hours equivalent to = 15.86 grams Cl.
Chlorine available = 7.93 grams.
Efficiency = 70.0 percent.
Percentage ring = 70.2 percent.
Percentage chain = 29.8 percent.

Experiment 12.—Ninety cc of toluene and 120 cc of concentrated hydrochloric acid were electrolyzed with direct current in a pear-shaped flask between vertical carbon electrodes of one-half inch diameter set about one and one-half inches apart and extending to the bottom of the flask. This flask was connected with a return condenser and heated on a sand bath to the boiling temperature of the liquid. The experiment was conducted in very diffused light.

Total silver chloride = 20.4192 grams.
Side chain silver chloride = 6.4854 grams.
Ring silver chloride = 13.9338 grams.
Total chlorine = 5.07 grams.
Six hours × 2 amperes = 12.0 amp. hrs.
Twelve ampere hours equivalent to = 15.86 grams Cl.
Chlorine available = 7.93 grams.
Efficiency = 63.9 percent.
Percentage ring = 68.2 percent.
Percentage chain = 31.8 percent.

Experiment 13.—Twenty-five grams of cold toluene were treated drop by drop with 6 grams of lead tetrachloride. Hydrochloric acid gas was evolved and could be detected by the odor. The toluene turned a beautiful red color, lasting several hours, but which finally disappeared, leaving the solution clear with a precipitate of white lead chloride in the bottom of the beaker. Some white precipitate was formed, together with the red color on adding the lead tetrachloride to the toluene. If the lead tetrachloride is added too fast, the reaction tends to become violent and the solution spatters.

On analysis the following results were obtained:

Total silver chloride = 0.9225 gram.
Side chain silver chloride = 0.0 gram.
Total chlorine = 0.229 gram.
Available chlorine (6 grams $PbCl_4$) = 0.61 gram.
Efficiency = 37.5 percent.

This experiment is analogous to that of benzene and lead tetrachloride.

Experiment 14.—Sixty-five cc. of toluene and twelve grams of anhydrous ferric chloride were placed in a round bottom flask, fitted with a return condenser and a thermometer, the bulb of which dipped into the toluene. This was placed in bright sunlight and slightly warmed from time to time. A brisk reaction took place beginning at 45° and varying from that to 60°. The odor of hydrochloric acid was very noticeable at the top of the condenser. After four hours, the flask was cooled and the liquid decanted off and filtered, giving a deep brownish black oil.

Analysis of 5 cc portion gave:

Total silver chloride = 0.2861 grams.
Side chain silver chloride = 0.0116 gram.
Percentage ring = 95.5 percent.
Percentage side chain = 4.5 percent.

The brown oil gave a blue color (Turnbull's blue) with potassium ferricyanide, thus showing the presence of ferrous iron.

The methods used in analyzing the products of the chlorination of toluene were as follows:

The total chlorine was determined with alcohol and sodium according to the method of Stephanow mentioned before. Usually five or ten cc of chlorinated toluene were added to 50 cc of alcohol. This was placed in a round bottom flask, fitted with a return condenser, and heated to boiling on the water bath. Sodium was then dropped into the solution, piece by piece, through the return condenser. A great excess of sodium was used, probably twenty-five times that required by theory. The heating was continued over a couple of hours and the liquid in the flask changed to a very viscous semi-solid condition. There was always some metallic sodium left at the end of a heating. After cooling, water was carefully added till the whole mass dissolved to a brownish yellow liquid; then dilute nitric acid and silver nitrate. Some tests on known amounts of chlorine substitution products showed this method to possess a very fair degree of accuracy when properly carried out.

Chlorine in the side chain was determined by prolonged boiling with alcoholic silver nitrate. The first precipitate of silver chloride was filtered off on a Gooch filter, the liquid then boiled again and the precipitate again removed and so on until no more silver chloride came down. This method also checked up very well when run with a known sample.

To get the addition chlorine, the filtrate from the above side chain determination was boiled with alcoholic caustic, then acidified with dilute nitric acid and excess of silver nitrate added. This is the same procedure that is used for benzene hexachloride.

Looking over the results obtained it is seen that at low temperatures and fairly high current density, the total efficiency is very low.

The experiments check quite well in regard to the percentage chain and ring substitution. There seems to be very little difference between very diffused light and absolute darkness.

The results obtained in Experiment 3 are of particular interest in that an extremely low current density was used. As a result it is seen that substitution takes place almost entirely in the ring, and also the efficiency is much higher than in the first two experiments with a higher current density.

The ordinary chemical method of getting chlorine into the ring with a compound such as toluene is to use a carrier and pass in chlorine with the toluene at a low temperature and in the dark. Evidently in Experiment 3 these results have been duplicated in a very satisfactory manner with the electric current. The work of a carrier has been duplicated electrolytically.

In the electrolytic chlorination of boiling toluene using the Oettel solution as a source of chlorine it is seen that the percentage of chlorine in the ring is about double that obtained at the temperature of melting ice with a corresponding current density (on account of the disintegration suffered by the carbon anode in Experiments 5 and 6, the results obtained therein will be disregarded for the present). Also the efficiency is much better, and as before there is very little difference in the results with very diffused light and absolute darkness.

Ordinarily, if chlorine is passed into boiling toluene, especially in the sunlight, substitution takes place largely in the side chain. On passing chlorine into boiling toluene, in ordinary diffused light, Cohen[1] obtained a result of ten percent to twenty percent in the ring, and ninety to eighty percent in the side chain.

Therefore, in the electrolytic chlorination of boiling toluene, it would be expected that a combination of these results and the effect of a carrier would be obtained, since it has already been found that electrolytic chlorine was similar to that obtained in the presence of a carrier. This is, in fact, what happens, as the results show a combination of the two effects and the amount of chlorine in the side chain is within a few percent of that in the ring.

In the experiments carried out by Cohen[1] on the electrolytic chlorination of boiling toluene results are obtained which differ from those found in this work, in that the chlorine goes into the ring to the entire exclusion of the side chain. Since he used a slightly different apparatus and concentrated hydrochloric acid as a source of chlorine it was thought that possibly this might account for the discrepancy between his results and those obtained in this work. Therefore, concentrated hydrochloric acid was substituted for the Oettel solution in the apparatus used in the preceding experiments and several runs were made.

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[1] Cohen-Dawson-Crosland: Jour. Chem. Soc., 87, 1034 (1905).

In the first of these, Experiment 9, the platinum anode was destroyed and the gas carbon substituted for it was largely disintegrated so that the experiment was repeated, using a graphite anode, which was found to suffer practically no disintegration. The results show a fairly good efficiency of chlorination and a slightly higher percentage of side chain chlorine in diffused light than in darkness. This was also noticed with the Oettel solution and is what should be expected. Although the side chain chlorine with the hydrochloric acid is about ten percent less than with the Oettel solution, it still amounts to a good percentage of the total chlorine substituted and by no means duplicates the results obtained by Cohen.

In looking around for the possible reasons for this discrepancy it was thought that the responsibility might be fixed on the different arrangement of the electrodes in the two cases. In these experiments the cathode was immersed in and exposed only to the liquid used as a source of chlorine. Correspondingly, the anode was exposed to come in contact, only with the toluene. In Cohen's apparatus the electrode consisted of two carbon rods in an upright position both extending down through the layer of toluene well into the liquid used as a source of chlorine.

Therefore, in Experiment 12 an apparatus was fixed up which resembled very closely that used by Cohen. The amounts of toluene, hydrochloric acid, and the current used were identical with amounts used by him. The results obtained agree very well with those in Experiments 10 and 11 in which the original apparatus was used. Thus, the discrepancy in results is not due to the form of the apparatus used. Therefore, the only possible reason for the difference in results would seem to be in the time over which the electrolysis was extended.

Cohen makes no statement as to the duration of the run nor as to the efficiency, but, judging from the quantity of chlorinated toluene obtained by him, the run must have extended over a considerably longer period than the time of these experiments, *i. e.*, six hours. This prolonged boiling introduces the possibility that the side chain chlorine first obtained was completely hydrolyzed, and on continued electrolysis practically all finally substituted in the ring. Again, unless he obtained an efficiency of one hundred percent, which is quite improbable, it is hard to see why any chlorine not substituted, but set free, would not go into the side chain as it would in the ordinary chlorination of boiling toluene with gaseous chlorine.

The theories and discussion given under the chlorination of benzene can be applied equally well to the chlorination of toluene. With toluene as with benzene, the hydrogen of the ring may be considered as negative in character. The side chain hydrogen of toluene may be considered as positive. Then, negative chlorine will displace ring hydrogen and positive chlorine, the hydrogen of the side chain.

It is known that if chlorine be passed in cold toluene in the presence of a carrier and very diffused light, substitution takes place in the ring almost entirely. Here, negative chlorine from the ferric chloride displaces negative hydrogen just as in the case of benzene. Under the same conditions of temperature and diffused light, electrolytic chlorine, which may be considered as negative, substitutes largely in the ring, especially at low current densities. Chlorine set free from an instable compound such as lead tetrachloride substitutes in the ring and not in the side chain. If lead tetrachloride be considered as breaking down according to the following equation,

$$PbCl_4 = PbCl_2 \text{ and } 2(Cl^-)$$

it is seen that the negative chlorine displaces the hydrogen of the ring just as in the corresponding case with benzene.

Again, the chlorine set free when toluene is treated with ferric chloride alone substitutes almost entirely in the ring, fully in accordance with the theory and parallel to the action with benzene. Thus, it is seen that electrolytic chlorine reacts toward toluene in the dark and at low temperature in a manner entirely analogous to ordinary chlorine in the presence of a carrier, or chlorine from instable chlor compounds. If ordinary gaseous chlorine is passed into boiling toluene in sunlight, substitution takes place almost entirely in the side chain. It may be considered that, at boiling temperature and in the light, dissociation of ordinary chlorine gas takes place into positive and negative chlorine. The positive chlorine may then displace the positive hydrogen of the side chain of the toluene, forming benzyl chloride. The hydrogen may unite with the negative chlorine and form hydrogen chloride.

In the electrolytic chlorination of toluene the efficiency at the higher temperature is several times as good as that obtained at lower temperatures, under similar conditions as to current density. The high side chain substitution in this case is probably due to the chlorine which had heretofore escaped as chlorine gas now substituting directly in the side chain in the same manner as ordinary chlorine at the higher temperature. This accounts for the higher efficiency obtained with boiling toluene than with cold toluene.

The chlorination of toluene was next studied under conditions similar to those necessary for the formation of addition products when applied to benzene. Toluene was chlorinated in the presence of dilute alkali, dilute acid and water.

Experiment 15.—One hundred cc of toluene and 75 cc of one percent sodium hydroxide solution were placed in a gas wash bottle and chlorine gas bubbled through for one and one-half hours,—very diffused light. The oil was then washed fifteen or twenty times with water in a separatory funnel or till no turbidity with silver chloride was observed in the wash water after the same had been standing in contact with the oil for some time. Ten cc portions were then removed for analysis.

The total chlorine was determined with sodium and alcohol according to the method previously described. The side chain chlorine was determined by boiling with alcoholic silver nitrate. The filtrate from this was treated with alcoholic caustic soda and boiled for some time, acidifying with dilute nitric acid and precipitating with silver nitrate.

In the case of benzene this treatment gives half of the addition chlorine, the other half substituting in the ring. With toluene this may give half, or perhaps some other fraction of the total addition chlorine, depending on how much substitution there has been previous to this treatment.

In any case it furnishes a means for comparing the relative amounts of addition chlorine obtained in a series of experiments with toluene, all performed under practically the same conditions. The substituted ring chlorine is, of course, obtained by difference.

In tabulating these experiments, the addition chlorine is put down as obtained by precipitation, and then for the sake of comparison, these results are multiplied by 2 as would be done in the case of benzene addition products. Percentage ring chlorine is obtained by taking twice the addition chlorine precipitated and adding to it the side chain chlorine and then subtracting this from 100.

One hundred cc toluene and 75 cc of one percent sodium hydroxide solution were placed in a gas wash-bottle and chlorinated for one and one-half hours,—diffused light, room temperature. There was a slight rise in temperature and the oil turned a yellow color.

Analysis of 10 cc.

Total silver chloride = 2.1081 grams.
Side chain silver chloride = 0.6312 gram.
Addition silver chloride = 0.4580 gram.
Percentage side chain = 30.0 percent.
Percentage addition precipitated = 21.75 percent.
Twice percentage addition precipitated = 43.50 percent.
Percentage ring by difference = 26.5 percent.

Experiment 16.—Same as in the preceding except that water was substituted for the caustic soda solution.

Total silver chloride = 1.3823 grams.
Side chain silver chloride = 0.3110 gram.
Addition silver chloride = 0.3195 gram.
Percentage side chain = 22.55 percent.
Percentage addition precipitated = 23.15 percent.
Twice percentage addition precipitated = 46.30 percent.
Ring percentage, by difference = 31.15 percent.

Experiment 17.—This experiment is identical with Experiment 15 except that a one percent hydrochloric acid solution was substituted for the caustic soda solution.

Total silver chloride = 1.3708 grams.
Side chain silver chloride = 0.3528 gram.
Additional silver chloride = 0.3832 gram.
Percentage side chain = 25.75 percent.
Percentage addition precipitated = 27.95 percent.
Twice percentage addition precipitated = 55.90 percent.
Ring percentage, by difference = 18.35 percent.

Experiment 18.—This experiment is identical with Experiment 15 except that it was carried out in absolute darkness.

Total silver chloride = 1.4505 grams.
Side chain silver chloride = 0.3412 gram.
Additional silver chloride = 0.3182 gram.
Percentage side chain = 23.5 percent.
Percentage addition precipitated = 21.9 percent.
Twice percentage addition precipitated = 43.8 percent.
Ring percentage, by difference = 32.7 percent.

Electrolysis of Sulphuric Acid—Insoluble Sulphur

It[1] has been shown that light will change sulphur which is dissolved and therefore soluble in carbon bisulphide into a modification which is insoluble in this solvent. Berthelot[2] has shown that when sulphuric acid is electrolyzed at high current density, sulphur is deposited at the cathode. He found this sulphur to be amorphous and insoluble in carbon disulphide. Heat changed it into the soluble variety. Berthelot obtained but very small quantities of this sulphur.

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[1] Rankin: Jour. Phys. Chem., 11, 1 (1907).
[2] Berthelot: Ann. Chim. Phys. [3], 49, 488 (1857).

Electrolysis of Sulphuric Acid

The following experiments were carried out under varying conditions of temperature, and the percentage of sulphur soluble in carbon disulphide was determined.

Experiment 1.—Concentrated sulphuric acid in a small beaker was electrolyzed between a platinum anode and a lead cathode (5 cm x 1 cm) at high current density (3 amperes), using a porous cup and keeping the beaker packed in ice. The temperature of the acid did not exceed 40°. About one-half of a gram of sulphur was obtained of which 65 percent was insoluble in carbon disulphide.

Experiment 2.—The run was repeated at a temperature of about 100° and practically all the sulphur was found to be soluble in carbon disulphide. Evidently by electrolysis some insoluble sulphur is formed provided the temperature be kept low. Of course, at a higher temperature this would be changed over to the soluble modification. Since it has been shown that light will change the soluble modification of sulphur over to the insoluble modification, and that by the electrolysis of sulphuric acid insoluble sulphur is obtained at the cathode, it is of interest to note that evidently there must be an analogy between the two processes by which this insoluble sulphur is produced, since the product of each process is the same.

Herschel's Work

In the Philosophical Transactions of the Royal Society for the year 1842 (page 201) is found a paper by J. F. W. Herschel describing the action of the solar spectrum on papers which had been impregnated with various substances more or less sensitive to light.

Herschel found that paper which had been washed in a solution of ferric chloride or ammonio-citrate of iron and potassium ferricyanide, thereby giving it a brownish green color, would, on exposure to light, become covered with a layer of Prussian blue. If the action of light be continued, the blue is replaced by white, which, in turn, takes on a brownish violet hue. He says that the whitening is obviously due to the de-oxidation of the precipitated Prussian blue and to the formation of the proto-ferrocyanuret of iron.

A number of experiments were performed for the purpose of duplicating these results electrolytically.

Experiment 1.—Filter paper or good "linen" paper was moistened with a solution of ferric chloride and potassium ferricyanide, giving it a light yellowish brown color. This was placed on a glass plate and two platinum strip electrodes brought into contact with it at a distance of about 3 cm from each other, and held down by suitable weights. On passing about 0.521 milliampere between these electrodes for a short time, a deep blue color is found under the cathode. The anode is either unchanged or turned slightly brown. On further electrolysis the cathode space turns white, and on still further electrolysis, this white changes to a brown color which is permanent. These reduction effects obtained under the cathode correspond exactly to the effects obtained by Herschel when he exposed paper similarly prepared to the action of sunlight. It is thus possible to make a series of electrolytic and solar prints which resemble each other very closely.

For instance, any desired figure, say the letter "C" can be cut out of a sheet of copper, and after being carefully polished, laid on a sheet of paper which has been impregnated with a solution made up of ferric chloride and potassium ferricyanide. Under this paper is a sheet of wet blotting paper, which, in turn, rests on a sheet of metal, that serves as the anode, the metallic "C" being the cathode. Using a low current density a blue "C" is very soon obtained which, after the paper has been washed with an excess of water, is permanent and resembles, in all respects, an ordinary blue print. The reaction takes place so quickly in this experiment that it is possible to write or draw pictures in blue, by simply using the end of the cathode wire as a pen and going over the paper prepared and arranged as above, in the same manner and at the same speed that would ordinarily be used with pen and ink.

Other light-sensitive papers were treated in this manner. Ordinary silver or "solio" paper was impressed with an electrolytic "C," the copper cathode having been plated with silver. After toning in the usual gold solution this "C" comes out a deep reddish brown color, exactly similar to a solar print.

Paper was treated with starch and allowed to dry. A solution of lead acetate was then poured over this starch paper and allowed to dry. The paper was then dipped in a strong solution of potassium iodide which caused the paper to take on a yellow color, due to the lead iodide formed. This sensitized paper was impressed with an electrolytic "C" which, after the paper had been allowed to remain in a strong solution of ammonium chloride, came out in a purple color due to the iodine set free. This is entirely analogous to the behavior of this paper in the sunlight.[1] From these results it is seen that the action of sunlight is similar to electrolytic reduction and *vice versa*. In other words, it is a case of actinic electrolysis.

Herschel describes further experiments in which paper was washed with a solution of ammonio-citrate of iron and exposed to light for different periods of time, and then treated with potassium ferricyanide. A sample of paper thus prepared was exposed for four or five seconds to sunlight. On bathing this in potassium ferricyanide solution a good Prussian blue color was obtained.

Another sample of paper so prepared was exposed for a very long time to the solar spectrum. When this paper was bathed in the potassium ferricyanide solution a most intense blue color was developed over the more refrangible region, in the interior of which the blue color appears to have been, as it were, eaten away, leaving a white oval; precisely the same phenomenon which would have been produced under the

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[1] Eder: Handbuch der Photographie, IV (4).

spectrum had the two liquids acted in conjunction. Herschel has thus shown that light first reduces ammonioferric citrate and then converts it into a reducing agent.

From these experiments it would seem that light reduces the iron of the ammonioferric citrate to the ferrous condition so that it gives a blue color with potassium ferricyanide, and at the same time oxidation of the ammonium citrate takes place with the consequent formation of a reducing agent. This reducing agent then acts on the potassium ferricyanide and reduces it to potassium ferrocyanide. A colorless compound is then obtained, which is the ferrous ferrocyanide or the proto-ferrocyanuret of iron mentioned by Herschel.

The following experiments were performed in order to determine whether it was possible by electrolytic oxidation to convert ammonium citrate into a reducing agent:

Reduction Through Oxidation

A solution of ammonium citrate was electrolyzed between platinum electrodes, at moderate current density, a porous cup being used. Silver nitrate was added to the anode compartment. After a few minutes the solution in the anode compartment darkened and a fine black precipitate came down. This can be shown to be metallic silver: by grinding in a mortar, also by dissolving in nitric acid and precipitating with hydrochloric acid. This shows that ammonium citrate can, by oxidation, be converted into a reducing agent and affords a further instance of the electrolytic duplication of photo-chemical reactions.

In a futher attempt to get a reducing agent through oxidation, bromine was slowly added to alcohol in the sunlight. A vigorous reaction took place and the odor of acetaldehyde was very noticeable. However, the liquid remained red in color and evidently there was some bromine and hydrobromic acid present for, on adding silver nitrate, a yellow-white precipitate of silver bromide came down. If any of the silver nitrate had been reduced to silver, this white precipitate completely masked it, as no metallic silver could be detected. Alcoholic silver nitrate was treated with bromine, but no better results were obtained.

Lecture Room Experiments

FURTHER EXPERIMENTS ON THE REDUCING ACTION OF LIGHT

Experiment 1.—A solution of ferric chloride and oxalic acid was added to a solution of potassium ferricyanide. This was diluted to a clear light yellow solution. A portion of this exposed to sunlight, burning magnesium ribbon, or arc light, turned blue almost at once. This indicates the reduction of ferric chloride to ferrous chloride and the subsequent formation with the potassium ferricyanide present of Turnbull's blue.

Experiment 2.—A few cubic centimeters of water were placed in a test tube and on this a layer of toluene. A few drops of bromine were then added and the whole shaken thoroughly, thus imparting a red color to the toluene. When this was exposed to a strong source of light, such as a burning magnesium ribbon, the toluene became colorless at once, thus showing the accelerating effect of light on the reaction between bromine and toluene.

Photo-Electric Experiments

ACTION OF LIGHT ON SILVER BROMIDE AND PLATINUM BLACK ELECTRODES IN VARIOUS ELECTROLYTES

Experiment 1.—Silver plates were covered with a layer of the bromide by making them anode in a solution of hydrobromic acid.

Two of these silver bromide electrodes were carefully washed and suspended in a solution of potassium bromide contained in a glass dish. The electrodes were connected to a sensitive low resistance galvanometer of the d'Arsonval type. A mirror was arranged so as to reflect a beam of sunlight on either one or both of the electrodes. If both electrodes were illuminated at once, the galvanometer moved either one way or the other as it was almost impossible to get the electrodes of exactly the same size and value.

On illuminating the electrodes separately it is found that which ever one is illuminated becomes the positive pole of the cell or the cathode.

Experiment 2.—If one electrode be dipped into a solution of erythrosine for a moment and then withdrawn and the excess of dye removed before the electrode is returned to the original potassium bromide cell, then on illumination of both electrodes the *undyed* electrode becomes cathode,—the dyed electrode being anode. If the undyed electrode is then dyed and replaced in the solution and both electrodes illuminated as before, the freshly dyed electrode is anode. And so the process can be repeated a great many times; in each case, the freshly dyed electrode is anode.

Experiment 3.—With platinum black electrodes in two beakers joined by an inverted U-tube, the illuminated dyed electrode becomes cathode,—just the reverse of the above effect. No effect was obtained with the electrodes undyed.

Experiments in photo-electricity have been carried out by many workers, including Becquerel, Minchin, Wilderman and others.

Minchin[1] covered silver plates with a layer of silver bromide and used two of them as electrodes in a solution of potassium bromide. He found that the electrode exposed to light became cathode. This result was duplicated in Experiment 1. The light seems to cause a reduction of the silver bromide, perhaps to a sub-bromide or finally to metallic silver. The bromine then is set free at or reacts with the electrode in the dark, *i. e.*, the anode.

Wilderman[2] repeated many of Minchin's experiments and studied some of them with much care. He found that the current always flowed from the electrode in the dark to the one in the light and that the cell was constant and non-polarizable so long as the film of silver halide on the cathode

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[1] Minchin: Phil. Mag. [5], 31, 208 (1891).

[2] Wilderman: Phil. Trans., 206A, 335 (1906).

had not been reduced to silver. When the cathode had been reduced to silver the cell became inconstant and polarized. By changing the cathode to the halogen compound again, the cell was completely restored. Wilderman thus explains the results of Minchin and the action of the cell in a satisfactory manner, but does not explain the results obtained when a sensitizer was used in the cell.

Minchin coated a silver plate with eosine and gelatine. On exposure to light he found that this plate became cathode in the cell. In another experiment he immersed two clean silver plates in a solution of eosine. In this case the plate exposed to the light became anode for a moment and then reversed to cathode. Wilderman has suggested that his reversal is due to polarization. The natural direction of the current is that first shown.

An experiment of considerable interest which Minchin performed was to immerse two silver bromide electrodes into a solution of potassium bromide and connect this cell with a source of electricity. The anode was visibly blackened by the passage of the current, but the cathode showed no visible change. However, on placing the cathode in pyrogallol developer it darkened in a manner similar to an ordinary exposed plate. There would seem to be a close analogy to the process taking place at the cathode and that which takes place on exposure to light.

It would seem that the effects obtained in the preceding experiments may be obtained as follows:

In Experiment 1 with two silver bromide electrodes in potassium bromide solution and one electrode illuminated, metallic silver is set free from the bromide at the illuminated electrode, making it cathode and the halogen travels as ion to the other electrode where it reacts to form more silver bromide.

Ag—AgBr KBr | KBr AgBr—Ag
Ag—Cathode
← Br

In Experiment 2 the dyed electrode becomes anode. Since it has been shown that by the action of light on sensitizers halogen is set free; in this case the halogen may react with the electrode forming silver halide and thus causing the electrode to become anode. Light acting on the undyed electrode, as in the preceding experiment, would tend to cause it to become cathode, thus adding to the effect produced at the dyed electrode. This double effect is, in a measure, opposed by the tendency of light to act on the silver halide of the dyed electrode and to precipitate silver in a manner similar to that on the undyed. However, the double effect mentioned above will always be greater than this and thus cause the dyed electrode to become anode.

Of course, when two silver bromide electrodes of the same size are illuminated, there is a tendency to precipitate silver on each electrode or, in other words, each electrode tends to become cathode, and they exactly oppose each other. Thus the E. M. F. due to the action of the halogen from the sensitizer would be that which would determine the direction of the current as is shown above.

In Experiment 3, with electrodes of platinum black, the dyed electrode becomes cathode. This effect is similar to that obtained by Minchin. This may be explained by the fact that light acting on erythrosine would tend to set the halogen free as in the preceding experiment. The halogen, in this case iodine, cannot react with the platinum electrodes as it did with the silver one in Experiment 2, so that in this case the action is an oxidizing one and the cell becomes an oxidation reduction cell.

(Pt) erythrosine——Erythrosine (Pt)
I
Reduction Oxidation
Cathode

From Minchin's experiment it is seen that reduction of silver halide at the cathode of an electrolytic cell will affect it in a manner similar to the action of light. In the same way in Experiment 1 it is seen that light acting on a silver halide electrode, generates an E. M. F. which sets up a current, indicating that at the electrode in question a reduction process is taking place. The E. M. F. generated by the action of light on sensitizers is in agreement with the fact that halogen is set free from them by the reaction of light.

These results do not throw any light on the action of sensitizers in a photographic plate. In the photographic plate the gelatine acts as a chemical sensitizer taking up halogen from the erythrosine, this latter then taking up halogen from the silver halide. The erythrosine thus acts as a halogen carrier. In the electromotive force experiments, there was nothing to absorb the halogen set free from the erythrosine and the direction of the current, therefore, depended on the reaction of the halogen.

Fluorescence

A series of experiments were carried out with the object of studying the chemistry of the reaction which takes place in fluorescent substances during exposure to light. In order to determine whether the fluorescence of various compounds was due to oxidation or reduction by light, these compounds were subjected to both chemical and electrolytic oxidation and reduction.

Experiment 1.—Uranium nitrate—water solution—also dilute nitric acid and dilute sulphuric acid solutions, 15 grams salt to 100 cc. of water were electrolyzed between platinum electrodes at varying current densities up to two amperes. The solutions were reduced to a green color but no fluorescence appeared. On being oxidized again with nitric acid in the dark no luminescence was observable.

Solutions of 20 grams of uranium salt in 100 cc of fifty percent sulphuric acid and also in ten percent nitric acid were electrolyzed between platinum electrodes in darkness at varying current densities, both alternating and direct, but no luminescence was observed.

Oxidation by Chemical Means

A solution of quinine sulphate in dilute sulphuric acid which had a good blue fluorescence was treated with solid sodium peroxide. The reaction went slowly at first and gradually increased in vigor. In a perfectly dark room it was possible to observe a well-defined greenish yellow luminescence, the intensity of which was proportional to the vigor of the reaction. With too great concentration of the sulphuric acid, the reaction went too fast and the luminescence was not apparent.

A number of blank experiments were run in dilute sulphuric acid without the quinine sulphate being present, but no luminescence was observed. The presence of the quinine therefore seems to be necessary for obtaining the effect. Sodium peroxide was added to cold water and the solution poured into quinine sulphate solution in the dark but no effect was observed. The same luminescence was observed when sodium peroxide was added to a dilute nitric acid solution of uranium nitrate.

Alkaline and acid solutions of eosine and fluorescein were treated in the same way without any results.

The best results were obtained with a fairly strong solution of quinine sulphate, not too acid, with sulphuric acid. This has a beautiful blue fluorescence in sunlight. On dropping a few grams of the powdered sodium peroxide into the quinine solution the reaction does not start at once, but only after five or ten seconds, and gradually increases in vigor, at the same time causing a luminescence which extends down into the solution and over an area of about 4 square centimeters. This experiment can hardly be taken to mean that the emission of fluorescent light is due to oxidation, since the effect seems to be obtained only when the solid salt acts on the solution and not when a solution of the sodium peroxide is poured into the quinine sulphate. The above solutions were each electrolyzed between platinum electrodes with direct current in a dark room but no luminescence could be observed.

FLUORESCENT SALTS IN SOLUTION TREATED WITH VARIOUS OXIDIZING AGENTS—PERSULPHATES

Quinine, uranium, fluoresceine, eosine, were each treated in turn with such oxidizing agents as sodium persulphate, ammonium persulphate, potassium persulphate and sodium perborate. The experiments were performed in a dark room, however, no luminescence was observable. The three persulphates did not decompose very rapidly. Manganous sulphate was added and while it seemed to cause more rapid decomposition of the persulphates, yet no luminescence was observed. The sodium perborate gives off oxygen quite readily, but causes no luminescence. It was first thought that, by direct oxidation or reduction of the fluorescent substance, luminescence might be obtained. Since this did not appear to be borne out by experiment, the possibility presented itself that certain rays might be evolved during the reaction of an oxidizing agent, which would excite a fluorescent body to luminescence. It was thought that perhaps when such oxidizing agents acted directly on solutions of fluorescent salts the fluorescent properties might have been destroyed. Thus, it would have been impossible to detect any luminescence which might have resulted from the rays evolved during the oxidizing action of the persulphates.

To overcome this difficulty the oxidation was carried out inside a quartz bulb tube, which was immersed in a fluorescent solution. The bulb tube was partially filled with dilute sulphuric acid and to this the solid persulphate was added. Thus the oxidation process was entirely separated from the fluorescent solution and still any rays of ultra-violet light which might be evolved could have access to the fluorescent solution.

Several experiments were performed, using this apparatus and adding various persulphates to the acid in the tube, however, no luminescence was observed in any case.

Several electrolytic experiments were carried out with this same quartz tube. It was partially filled with dilute sulphuric acid and into this two lead wire electrodes were immersed. The quartz tube was then suspended in a beaker of fluorescent solution. Thus in case any rays of an ultraviolet nature or rays which could in any way affect a fluorescent solution were emitted during oxidation or reduction processes at the electrodes, they would have a chance to act on the fluorescent solution. The fluorescent solution, not being subjected to electrolytic oxidation or reduction, would remain unchanged and its fluorescent properties would be unimpaired.

When the lead electrodes were connected to alternating current, luminescence was observed. It was found that the luminescence was at the electrodes themselves and did not in any way depend on the fluorescence of the solution surrounding the quartz bulb.

Therefore, in the experiments described below, the quartz bulb was not immersed in the fluorescent solution.

Experiment.—Very dilute sulphuric acid was electrolyzed in a dark room with lead wire electrodes and alternating current,—60 cycles, 3 amperes, 2 amperes, and 1 ampere. Both electrodes take on a pale greenish yellow luminescence. The solution fills up with a fine white precipitate—lead sulphate—which obscures the electrodes, but by diffusing the light causes the whole solution to glow. The appearance of the luminescence is coincident with the passage of the current and seems to depend on the intensity of the current as three amperes gave a better effect than one ampere. Also the greater the current density, the quicker the solution fills up with the white precipitate. The lead electrodes were replaced with platinum wires, but no luminescence was observed. This also precludes the possibility of the luminescence having been caused by a static discharge between the electrodes. With lead electrodes and direct current the luminescence was not observed. The anode becomes covered, almost immediately, with a layer of brown lead peroxide, and the solution does not fill up with the white precipitate. During electrolysis of the dilute acid with alternating current the lead electrodes were dissolved at a fairly rapid rate.

Electrolysis of Fluoresceine

A solution of fluoresceine weakly alkaline with sodium hydroxide was electrolyzed between platinum strip electrodes with porous cup, two amperes, direct current, temperature 25° and 50°. Apparently more gas comes off from the cathode than the anode. The cathode solution where filled with gas seems to take on a brick-red tinge, and on turning off the current, the red color slowly disappears and with it the gas held in suspension in the solution. This entire effect may be due to the gas held in suspension in the solution. After a while the cathode solution becomes lighter in color. Two samples, one from the anode and one from the cathode, if allowed to stand exposed to the air, tend to assume a common color. In the anode compartment the tendency is to deepen the color, if anything, but not the fluorescence. Eosine behaves much the same way.

After running some time the cathode solution is pretty well bleached out retaining a very slight pink color and fluorescence. After electrolyzing, to this extent, the anode solution is deepened in color and samples removed from each compartment and allowed to remain exposed to the air, do not assume their original color within any reasonable time. However, it is doubtful whether these experiments prove anything, as no fluorescence is destroyed nor is any fluorescence created or increased in intensity. Nor is the color on reduction changed to a green or yellow fluorescent shade as the case may be. The cathode effect can be duplicated by taking some of the original solution and diluting with water.

If a solution of eosine is treated with sodium peroxide a practically colorless solution results. This solution was treated with dilute nitric acid, then with silver nitrate and the amount of precipitated silver bromide determined.

	$C_{20}H_8Br_4O_5$ eosine (hot)	Eosine (cold)	Sodium salt eosine (cold)
Weight sample	0.2823	0.2398	0.1679
AgBr precipitated	0.2518	0.2206	0.1146
100 % bromine as AgBr	0.3275	0.2785	0.1828
Percent bromine precipitated	76.8	79.2	62.6

From these results it is evident that a large part of the bromine in eosine is set free on treatment with sodium peroxide, *i. e.*, on oxidation.

The experiment was next tried of treating eosine and erythrosine with a reducing agent such as hydrogen evolved from zinc dust and sodium hydroxide. The solution of the dye is quickly changed to a colorless solution without any fluorescence. As before, these solutions were tested for the amount of halogen set free. Temperature = 25°.

	Eosine	Erythrosine
Weight sample	0.1507	0.0944
AgBr or AgI precipitated	0.0261	0.0259
100% halogen salt	0.1746	0.1065
Percent halogen precipitated	14.95	24.3

From these results it is seen that some halogen is set free on the reduction of eosine or erythrosine.

Eosine, erythrosine or fluorescein can be reduced to a colorless solution with zinc dust in sodium hydroxide. On exposure to sunlight this solution immediately changes to a colored fluorescent solution. A sample of any one of the above which has been reduced to a colorless solution with zinc and sodium hydroxide will not change to a colored solution on standing in the dark, at least within a space of twenty-four hours.

A solution of erythrosine in water does not fluoresce to an appreciable extent. If the colorless solution, obtained by the reduction of an erythrosine solution, is placed in the sunlight, it takes on a pink color together with a green fluorescence. This will also take place in a tightly stoppered bottle with all air excluded, though in this case, the red color precedes the fluorescence. If some of the colorless solution be diluted and allowed to stand in a beaker in the sunlight for some time the solution takes on a beautiful greenish colored fluorescence much resembling fluoresceine. Thus, a non-fluorescent liquid is changed to a fluorescent one.

Eosine behaves in practically the same way except that it is, of course, fluorescent before reduction. However, the final fluorescence obtained after exposure of the reduced solution to sunlight more resembles fluorescein than eosine.

Fluoresceine behaves exactly as the two solutions mentioned above.

From the preceding experiments it is seen that the fluorescence of a solution can be destroyed by oxidation or reduction. In the case of reduction the effect of light is to restore the fluorescence.

The foregoing experiments would seem to indicate that the fluorescence of a substance is not due to a simple oxidation or reduction but evidently consists of a reaction of more complicated nature.

Action of Sunlight on Sensitizers

Erythrosine and Water.—Two solutions of different concentrations were made up and portions of each placed in two small glass stoppered bottles with as little air present as possible. One set of bottles was placed in sunlight and the other set in the dark. The more dilute solution of erythrosine bleached in a few hours in the sunlight and the other one bleached after a couple of days. The solution in the dark remained unchanged. Filter paper dyed with erythrosine and exposed to light bleached after a few hours. Porous porcelain plates dyed with erythrosine bleached after a few days.

The solution which had been bleached in sunlight gave a small amount of white precipitate with silver nitrate.

A solution of erythrosine, water and potassium arsenite, was made up and placed in glass stoppered bottles, and one sample exposed to sunlight and the other placed in the dark, as in the preceding case. In the sunlight the solution quickly takes on a light brown color with a green fluorescence. The samples in the dark remains unchanged. An alcoholic solution of eosine bleaches very slowly in sunlight.

A solution of erythrosine, water and sodium sulphite changes to a light yellowish brown with a green fluorescence when exposed to sunlight. In darkness there is no change.

A solution of erythrosine, water, sodium hydroxide and sodium sulphite gives a deep red solution with green fluorescence when exposed to sunlight. When compared with a sample which has been allowed to remain in the dark it is found that the red color has deepened considerably in the sunlight. The solution in the dark has not changed.

A solution of erythrosine, water and sodium thiosulphate, also the same solution with sodium hydroxide added, both changed to a deep red color in sunlight without any fluorescence. In the dark there is no change.

The above experiments on the action of light on organic dyes in the presence of reducing agents were prompted by the work of E. Vogel.[1] He treated solutions of erythrosine with hydroxylamine hydrochloride and sodium hydroxide, with sodium hydroxide alone, and also with hydrogen peroxide. A portion of each solution was exposed to sunlight and the other portion kept in the dark. After a short exposure to sunlight the solutions had changed as follows:

The hydrogen peroxide solution showed no visible change.

Sodium hydroxide solution had bleached a little.

The neutral solution had bleached a little.

The solution containing hydroxylamine was entirely changed; the tetraiodfluoresceine had been reduced to ordinary fluoresceine.

Vogel found that all the bromine and iodine substituted eosine dyes behaved like erythrosine. The experiments cited in this paper confirm the work of Vogel.

Reducing agents such as sodium arsenite and sodium sulphite when mixed with erythrosine and exposed to light caused the reduction to take place very quickly. The experiments show conclusively that organic dye stuffs can be reduced by light.

Potassium permanganate added to solutions of eosine

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[1] Vogel: Wied. Ann., 43, 462 (1891).

and erythrosine exposed to sunlight for several days give a flocculent brown precipitate in the bottom of the beaker and a clear supernatant liquid. This clear liquid gives a precipitate with silver nitrate showing that some halogen has been set free.

Several glass plates were coated with gelatine, dyed with erythrosine and exposed to sunlight for several weeks, one-half of each plate being carefully protected from the light.

On some of the plates the dye was made slightly alkaline with ammonia and others had small amounts of ammonium bromide present with and without ammonium hydroxide. A set of these plates was exposed to the sunlight, in a suitable glass bottle filled with hydrogen, thus eliminating any effect which the oxgyen of the air might have on the dye.

Abney exposed a gelatine plate dyed with cyanine to the light, then coated it with silver bromide emulsion in the dark and succeeded in developing the plate. The object of the above experiments was to duplicate the results of Abney, using the sensitizer erythrosine instead of cyanine. In all cases the part of the plate exposed to the light bleached after several weeks of exposure. Some plates were given an exposure of only a few hours.

The plates containing ammonium bromide were immersed for a few minutes in a bath of silver nitrate which, of course, precipitated silver bromide in the gelatine. They were then developed in a slow developer but no difference in the two halves of the plate could be detected. The plates which did not contain the ammonium bromide, were first immersed in a bath of either ammonium or potassium bromide, then in silver nitrate and developed as before. The results were equally unsatisfactory.

From the results of these experiments it is seen that when light acts on a sensitizer, such as erythrosine, it bleaches it and sets free some halogen. When the sensitizer is in the presence of a reducing agent, such as sodium sulphite or arsenite the clear red solution of erythrosine takes on an appearance much resembling fluoresceine. This reaction takes place so quickly that it can be performed as a lecture experiment by using an arc light or magnesium ribbon as a source of light. The reaction here seems to be the same as that described in a preceding experiment where the erythrosine was reduced to a colorless solution with zinc and sodium hydroxide and afterwards, on exposure to light, took on a color and fluorescence resembling fluoresceine. Halogen was also set free in this case.

When a sensitizer is oxidized halogen is set free, though with a strong oxidizing agent like potassium permanganate it is probable that decomposition takes place.

Summary

The general results of this paper are:

(1) The rate of the reaction between ferric sulphate and copper is dependent on the rate of diffusion of the liquid. Ordinary means of measurement do not show the reaction to be of a photo-chemical nature.

(2) The electrolytic chlorination of acetic acid is unsatisfactory. Electrolytic chlorine is different in character from that due to the dissociating influence of sunlight on ordinary chlorine.

(3) The electrolytic chlorination of benzene is satisfactory from a standpoint of efficiency. The chlorine obtained by electrolysis is similar in action to ordinary chlorine in the presence of carriers such as ferric chloride, at low temperature and in diffused light or darkness.

(4) Chlorine from such instable compounds as lead tetrachloride acts in a manner similar to electrolytic chlorine, displacing the hydrogen of the benzene ring.

(5) Benzene can be chlorinated by the direct action of ferric chloride, provided the two are heated together and exposed to sunlight.

(6) Experimental facts in the chlorination of benzene in the presence of a carrier indicate a displacement of the hydrogen of the ring by the halogen and subsequent forma-

tion of hydrogen halide. Facts are opposed to the formation of addition compounds between the benzene and the carrier.

(7) With toluene, chlorine obtained electrolytically, or from instable compounds such as lead tetrachloride or from ferric chloride, substitutes in the ring at low temperatures. At higher temperatures electrolytic chlorine also substitutes in the side chain.

(8) Sulphur obtained by the electrolysis of sulphuric acid is similar to that precipitated from a solvent by the action of light.

(9) Many of the photo-chemical experiments of Herschel have been duplicated electrolytically.

(10) It has been shown that, by oxidation, ammonium ferric citrate can be converted into a reducing agent.

(11) In the cases studied, fluorescence is not the result of a simple chemical oxidation or reduction, but is apparently due to a more complicated reaction.

(12) In the electrolysis of dilute sulphuric acid with alternating current and lead electrodes a luminescence is obtained extending over each electrode.

(13) The action of solid sodium peroxide on a solution of quinine sulphate is accompanied by a luminescence.

(14) Photo-electric experiments show that light tends to set halogen free from a sensitizer.

(15) If a sensitizer, such as eosine or erythrosine, be reduced and allowed to stand in sunlight it is converted into a fluorescent substance.

(16) If a sensitizer, such as eosine or erythrosine, be exposed to light in the presence of a reducing agent it is very quickly converted into a fluorescent substance.

(17) Experiments show that organic dyes can be reduced by light.

(18) The results obtained in this work agree with and tend to confirm the Grotthuss theory of the action of light.

This work was suggested by Professor Bancroft and carried out under his direction.

The author takes this occasion to express his appreciation of the many suggestions received from Professor Bancroft and of his very generous interest in the work.

Thanks are also extended to Professor Orndorff and to Dr. Delbridge of the Department of Organic Chemistry for interest taken in the work and for the use of materials belonging to that department.

Cornell University,
June, 1908.

THE INDUCTION BY FERROUS SALTS OF THE REACTION BETWEEN CHROMIC AND HYDRIODIC ACIDS.

BY ROSS A. GORTNER

The reaction between chromic acid, ferrous salts and hydriodic acid, studied here some years ago by Miss C. C. Benson,[1] presents many points of interest which invite further investigation: the great influence of the acid concentration on the rate, the retarding action of ferric salts, and the observation that less iodine is liberated per second at 30° C than at 0° C, are all most unusual. Mr. Green's work on catalysis by ferric salts, recently published,[2] which shows that nothing similar to the retardation observed by Miss Benson is to be met with in the behavior of reactions otherwise closely analogous, adds interest to this exceptional case.

My own measurements, described in the present paper, show that the lessened retardation observed when "aged" portions of the oxidation product were added to the reaction mixture is quantitatively ascribable to the hydrolysis of the ferric salts, and that colloids and colloidal ferric hydrate in particular have but little effect on the rate. Sulphuric acid may be replaced by hydrochloric acid without changing the general nature of the results, but the addition of fluorides, chlorides or bromides retards the liberation of iodine and accelerates the oxidation of the ferrous salt. This observation may be accounted for very naturally by an explanation in keeping with Miss Benson's Ferroiodion theory; it may therefore be regarded as furnishing independent evidence in support of the latter. Miss Benson's observation that the rate of liberation of iodine at 30° C is less than at 0° C, is confirmed and supplemented by experiments which show that the rate of oxidation of the iron is greater at the higher temperature.

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[1] Jour. Phys. Chem., 7, 1 (1903); 7, 356 (1903); 8, 116 (1904).

[2] *Ibid.*, 12, 389 (1908).

Method of working and of recording the results

In the composition of the solutions, in the methods of manipulation, and in the temperatures worked at, I closely followed the details described by Miss Benson;[1] and after a little practice found that on repeating her experiments I obtained identical results. In tabulating the measurements, also, the symbols and arrangement described on page 359 of the paper referred to have been adopted;[2] for convenience it may be repeated here that the numbers after the symbols Ac, Cr, KI, Fe, are very closely proportional to the number of equivalents of the various reagents present in the reacting solution—one formula-weight of bichromate being equivalent to seven of sulphuric acid and to six of ferrous sulphate or potassium iodide.

To facilitate reference, my tables and experiments are numbered consecutively with those of Miss Benson's last paper.

Effect of chlorides, bromides, and fluorides on the rates

When hydrochloric acid is substituted for sulphuric acid (Table XXXVI) *the rate of liberation of iodine is somewhat reduced,* but still remains proportional to a high power of the concentration of the acid. The retardation cannot be ascribed to the action of the ferric salt, for, as is shown on page 636, ferric chloride and ferric sulphate have the same effect on the rate; it is explained by the experiments of Table XXXVII, which show that addition of sodium chloride, potassium bromide, or potassium fluoride reduces the rate of liberation of iodine; potassium sulphate is without effect.

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[1] Ac 10 represents 10 cc of 0.059 F sulphuric acid (*i.e.*, acid containing 0.059 formula weights H_2SO_4 per litre); Cr 10, 10 cc of 0.0083 F potassium bichromate (including unreduced bichromate, if any, in the oxidation product); KI 10, 10 cc of 0.0479 F potassium iodide; Fe 1, 10 cc of 0.05 F ferrous sulphate; Ox 5, the product of oxidation of 5 cc of 0.05 F ferrous sulphate. The duration of the reaction in minutes is entered in the tables under Θ; the number of cc of N/100 sodium arsenite equivalent to the iodine liberated, under As; and the number of units of ferrous salt oxidized, under x, 10 cc 0.05 F ferrous salt being taken as the unit. As = $5y$.

[2] Jour. Phys. Chem., 7, 357 (1903).

The measurements of Table XXXVIII[1] show that *the rate of oxidation of iron is increased* by addition of fluoride. These observations may be explained very naturally by assuming that the halogen and the ferro-ion unite to form a complex FeF' (analogous to the ferroiodion FeI' of Miss Benson's hypothesis);[2] this substance on oxidation would yield ferric salt but no iodine, the induction factor should therefore fall off with increase in the concentration of the fluoride, as observed. To account for the increased rate of oxidation of the iron, it is only necessary to assume that the complex FeF' is more rapidly oxidized than Fe'' (or FeI').

The effect of colloids on the rate

The fact that under certain circumstances ferric hydrate can exist in the colloidal form, suggested experiments with other colloids. Agar-agar in one-tenth percent solution has no effect. Egg albumen, two-tenths percent solution, retards the oxidation, but this is probably due to its action as a weak base,[3] the retardation being proportional to the amount of albumen used. "Dialyzed iron" (colloidal ferric hydrate) retards a little, but nothing like as much as the same quantity of ferric sulphate or chloride—see Table XXXIX.

On the whole, therefore, the colloids experimented with have no retarding action to be compared with that of the ferric salts.

Diminished retardation by "aged" ox. prod.

When the product of oxidation of ferrous sulphate by chromic acid (ox prod) is allowed to stand, it gradually de-

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[1] The values of x in this and other tables of this paper are obtained by interpolation from the data of part B of the table, as explained in this Journal, 7, pp. 3 and 364 (1903).

[2] Undissociated FeI_2, FeF_2, etc., or the corresponding acids might be assumed; the type of the reaction however is fixed by Miss Benson's measurements. See Jour. Phys. Chem., 11, 9 (1907). W. L. M.

[3] Ber. chem. Ges. Berlin, 28, Ref. 858 (1895).

posits a yellow brown precipitate and its retarding power is lessened.[1] Similar changes in solutions of ferric chloride have been studied by Goodwin,[2] who showed by conductivity measurements that the "ageing" of the solutions was due to hydrolysis. In solutions of the strength of my "ox prod" this hydrolysis is accompanied by the formation of a precipitate, so that the concentration of the ferric salt is reduced, and that of the acid is increased—both changes tending to accelerate the liberation of iodine. The experiments of Tables XL and XLI show that the increased rate actually observed when "aged" ox prod is used can be completely accounted for if these changes in acidity and ferric concentration are taken into consideration.

In these experiments, three ferric solutions were used. The first was that employed in most of my work at 0° and is referred to in the tables under the title "Ox": it was prepared fresh by making up 200 cc acid, 600 cc bichromate and 20 cc ferrous sulphate (the undiluted solutions were used) to two liters; 50 cc contained the oxidation product of 5 cc decinormal ferrous sulphate, and in addition, 10 cc F/120 bichromate unreduced,[3] but no free acid. The second was prepared from the first by boiling for about half a minute, filtering hot and cooling; the third was obtained by allowing some of the first to stand 64 days at room temperature and filtering. The ferric salt in each of these three was determined volumetrically. by stannous chloride and bichromate; the bichromate was determined by titration with ferrous sulphate; and the acid by adding excess of volumetric potassium hydrate, and titrating back with sulphuric acid (without filtration) using methyl orange as indicator. The last determination gave both the free acid and that combined with the ferric salt; the latter was calculated from the ferric determination and subtracted. Fifty cc of each of the three preparations contained respectively:

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[1] Jour. Phys. Chem., 7, 362 and Table 15 pp. 384.

[2] Zeit. phys. Chem., 21, 1 (1896).

[3] Jour. Phys. Chem., 7, 359 (1903).

	I	II	III
Ferric salt	5.0	1.0	2.87
Bichromate	10.0	10.0	10.0
Free acid	0.0	5.0	2.6

in the units defined on page 633.

In Table XL the volume and the distinguishing number of the ferric solution used in each experiment is given under Ox, also the ferric salt and the free acid contained in it ("Ac from Hydrol"); under "acid added" is entered the amount of acid from the stock solution; the "total acid" is obtained by adding the last two.

Hydrolysis of the ferric solution (ox prod) can be completely prevented by making it up with excess of acid instead of with excess of bichromate; and further experiments (Table XLI) show that an acid solution of ferric chloride may be substituted without affecting the rates. The solutions used contained, in 50 cc:

	IV	V
Ferric (sulphate)	5.0	0.0
Ferric (chloride)	0.0	5.0
Free acid	10.0	10.0
Bichromate	0.0	0.0

Experiments at 30.5° C

Miss Benson has shown that by titrating as directed on page 357 of her paper, the amount of iodine liberated by the reaction may be determined accurately if both reaction and titration are carried out at 0° C; experiments of my own confirm this conclusion. At 30° C, however, owing no doubt to the fading of the blue color of iodide of starch at high temperatures, a considerable excess of iodine—from 0.6 to 0.8 cc N/100 iodine in the 700 cc of solution—is necessary to produce the permanent tint taken as end point. When any arsenite was required in the "blank" experiment (without ferrous salt) the same correction for the end point would apply there; and in these cases the net arsenite (after subtracting the "blank") would be free from error. When "As $\doteq 0$" in the blank experiment however, *i. e.* when the iodine liberated in the blank experiment was less than enough to give the blue with starch, the numbers are too low. This is the case with most of Miss Benson's measurements from Table XXIV onward. I have consequently repeated the determinations at 30° C; the results are contained in Tables XLV to XLIX. While confirming Miss Benson's conclusions as to the effect of the concentrations of the various reagents on the rate of liberation of iodine, they show that the rate of oxidation of the iron in the solution is much more rapid at the higher temperature, and that in many cases all the iron is oxidized within two minutes; this result was checked by addition of potassium ferricyanide.

The correction for the end point (which in all the tables has been added to the observed numbers before entering them under "As") is given at the head of each table; it varies slightly from case to case, and was obtained as follows: The amounts of acid, bichromate, and "ox. prod." indicated at the head of the table were mixed at 30° C with water and 10 cc of a saturated solution of iodine in water, the ferrous sulphate was then added with enough water to bring the whole to a volume of 700 cc; one minute later ammonium bicarbonate was added, then 5 cc normal potassium iodide, and starch, and then N/100 arsenite to the "end point." In order to find the arsenite equivalent of the iodine employed, 10 cc of the same iodine solution was then added, and arsenite to the end point again; in every case 1.90 cc arsenite was required. Table XLII shows that the "correction" does not depend on the length of time the reacting solution remained in the bath, loss of iodine from evaporation is therefore not to be feared.

The induction factor at 0° and at 30°

Miss Benson has shown[1] that the induction factor—or

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[1] Loc. cit., page 369.

the number of equivalents of iodine liberated per equivalent of iron oxidized—varies, at 0° C, from 1.2 to 1.8. To make the evidence for this as clear as possible, I have calculated the induction factor, *viz.*, the fraction y/x, from the data of her Table XVII, and present the results in Table XLIII. At 30° the induction factor is much lower than at 0°; as shown in Table XLIV it falls as low as 0.4, and never rises above 1.0.

The influence of the concentrations of the various reagents on the factor is in accordance with the supposition[1] that both Fe'' and FeI' (FeI_2, etc.) are simultaneously undergoing oxidation in the solution; increase in the concentration of the acid, for instance, affects the rate of the second reaction much more than that of the first,[2] and consequently increases the induction factor. A quantitative test of this assumption is postponed until conductivity measurements furnish data for a plausible assumption as to the formula of the addition product (see foot-note, page 634).

My thanks are due to Professor W. Lash Miller, at whose suggestion these measurements were carried out in the Winter of 1907–8.

Table XXXVI (Hydrochloric Acid)

Cr, 20; KI, 20; Ox, 5; Fe, 1.0; V, 700; t, 0° C

	Expt. 49 HCl, 10	Expt. 5a[3] H_2SO_4, 10	Expt. 50 HCl, 20	Expt. 9a[3] H_2SO_4, 20
θ	As	As	As	As
0.25	—	—	2.35	4.05
1.0	1.35	1.90	—	7.15
2.0	2.35	3.10	7.70	8.00
4.0	3.90	4.30	—	—

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[1] Loc. cit., p. 374.

[2] Ibid., p. 366.

[3] In Expts. 5*a*, 9*a*, etc., the composition of the solution was the same as in Miss Benson's Expts. 5, 9, etc.

TABLE XXXVII (SALTS)

Ac, 10; Cr, 20; KI, 20; V, 700; t, 0° C

Expt.	Salt added	Ox	Fe	θ	As	Blank	No. of blank Ex.
51	0.88 g. K_2SO_4	0	1.0	1.0	4.90	5.00	23*a*
52	0.5 g. NaCl	0	1.0	0.5	3.30	3.90	23*a*
53	do	0	0.5	0.5	2.30	2.60	54
55	1.0 g. NaCl	0	1.0	0.5	2.85	3.90	23*a*
56	do	0	0.5	0.5	2.10	2.60	54
57	1.0 g. KBr	0	1.0	0.5	3.30	3.90	23*a*
58	0.03 g. $KF.2H_2O$	5	1.0	4.0	4.40	4.35	5*a*
59	0.1 do	5	1.0	4.0	4.25	4.35	5*a*
60	0.5 do	0	1.0	1.0	0.80	5.00	23*a*
61	1.0 do	0	1.0	1.0	0.20	5.00	23*a*

TABLE XXXVIII (POTASSIUM FLUORIDE)

Ac, 10; Cr, 20; KI (after θ), 20; Ox, 0; V, 700; t, 0° C

	Expt. 62 KF, 0		Expt. 63 KF, 1.0[1]		Expt. 64 KF, 3.0		Expt. 65 KF, 5.0		Expt. 66 KF, 10.0	
θ	As	x	As	x	As	x	As	x	As	x
0.25	3.20	0.65	2.80	0.71	1.60	0.82	0.75	0.90	0.15	0.98
0.50	2.35	0.75	1.80	0.83	0.80	0.91	0.30	0.96	—	—
1.0	1.60	0.84	1.15	0.90	0.40	0.95	—	—	—	—
2.0	1.05	0.90	0.60	0.94	—	—	—	—	—	—
4.0	0.60	0.94	—	—	—	—	—	—	—	—

TABLE XXXVIII B

Fe	KF, 0 As	KF, 1.0 As	KF, 3.0 As	KF, 5.0 As	KF, 10.0 As
1.0	7.20	7.70	7.80	6.20	5.40
0.8	6.15	6.55	6.35	5.20	....
0.6	5.10	5.20	....	4.20	3.60
0.4	3.60	3.70	3.50	2.90	....
0.2	2.00	2.10	1.80	1.60	1.40
0.1	1.00	1.05	0.90	0.80	0.70
0.0	0.00	0.00	0.00	0.00	0.00

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[1] KF, 1.0 indicates 10 cc of a solution containing 0.33 gram of potassium fluoride, $KF.2H_2O$ per litre, and is approximately one F-wt of fluoride for one of ferrous salt in the reacting solution.

TABLE XXXIX (COLLOIDS)

Ac, 10; KI, 20; Fe, 1.0; V, 700; *t*, 0° C

Expt. 67 Agar-agar[1] Cr, 20; Ox, 5; θ, 4.0		Expt. 68 albumen[2] Cr, 20; Ox, 0; θ, 1.0		Expt. 69 Dialyzed iron[3] θ, 1.0				
Agar	**As**	**Albumen**	**As**	**Cr**	**Ox**	**Dial**	**Total Fe'''**	**As**
0	4.40	0	5.05	10	0	0	0	2.40
5 cc	4.35	50 cc	2.25	10	0	5 cc	10.8	2.00
25	4.48	100	1.15	10	5	0	5	0.80
50	4.40	150	0.55	20	0	0	0	5.05
100	4.40	—	—	20	0	5 cc	10.8	3.50
—	—	—	—	20	5	0	5	1.90

TABLE XL ("AGED" OX PROD)

KI, 20; Cr, 20; Fe, 1.0; V, 700; *t*, 0° C; θ, 1.0

Expt.	Ox	Fe'''	Ac from hydrol.	Ac added	Total Ac	As
70	0	0	0	15	15	7.30
71	5 II	1.0	5.0	10	15	6.70
72	1 I	1.0	0	15	15	6.65
73	5 III	2.87	2.6	10	12.5	4.60
74	2.87 I	2.87	0	12.6	12.6	4.00
75	10 II	2.0	10	0	10	3.20
76	2 I	2.0	0	10	10	3.05
77	0	0	0	0	0	0.00
78	5 I	5.0	0	0	0	0.00
79	0	0	0	10	10	5.05
5*a*	5 I	5.0	0	10	10	1.90
80	10 III	5.74	2.6	0	2.6	0.15

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[1] One-tenth percent solution of agar-agar.

[2] One-fifth percent solution of egg-albumen.

[3] 5 cc of the dialyzed iron solution contained 10.8 units.

TABLE XLI (ACID OX PROD)

Ac, 20; Cr, 20; KI, 20; Ox, 5; Fe, 1.0; V, 700; *t*, 30.5° C; Corr, 0.75

Expt.	θ	Ox	As
81	0.25	0	3.35
"	0.50	0	4.05
"	1.0	0	4.70
"	2.0	0	5.25
82	0.25	5 IV	1.35
83	0.25	5 V	1.30
84	0.25	5 I	1.35
82	0.50	5 IV	2.00
83	0.50	5 V	1.90
84	0.50	5 I	2.10
82	1.0	5 IV	2.85
83	1.0	5 V	2.85
84	1.0	5 I	2.85
82	2.0	5 IV	3.85
82	1.0	5 IV[1]	2.85
83	2.0	5 V	3.85
84	2.0	5 I	3.85

TABLE XLII (CORRECTION FOR END POINT AT 30° C)

Expt. 85: Ac, 20; Cr, 20; Ox, 5; Fe, 1.0; V, 700; Iodine 10 cc = As 1.90; *t*, 30.5° C

θ	As found	Corr.
0.25	1.15	0.75
0.50	1.15	0.75
1.0	1.15	0.75
2.0	1.10	0.80
4.0	1.15	0.75
8.0	1.05	0.85

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[1] Boiled.

TABLE XLIII

(Values of the Induction factor, y/x, calculated from Miss Benson's measurements at 0° C; see her Table 17)

Cr, 20; V, 700; t, 0° C; Ox, 5 except in Expt 23 Ox, 0

Expt.	Ac	KI	Fe	Induction factor					
				$\theta = 0.5$	1.0	2.0	4.0	8.0	∞[1]
5	10	20	1.0	$y/x = 1.4$	1.4	1.3	1.4	1.4	1.5
6	10	20	0.5	1.3	1.4	1.4	1.4	1.4	1.6
9	20	20	1.0	1.6	1.6	1.6	1.7	1.8	1.8
14	10	5	1.0	—	0.9	0.9	0.9	1.0	1.2
15	10	5	0.5	—	—	1.1	1.1	1.2	1.4
16	10	10	1.0	—	0.7	0.8	1.1	1.2	1.4
17	10	10	0.5	—	1.2	1.3	1.4	1.6	1.7
23	10	20	1.0	1.4	1.5	1.4	1.4	—	1.5

TABLE XLIV

(Values of the Induction factor, y/x, at 30.5° C; from Tables 45–49)

Fe, 1.0; t, 30.5° C; V, 700

Expt.	Ac	Cr	KI	Ox	Induction factor				
					$\theta = 0.25$	0.5	1.0	2.0	4.0
86	10	20	20	0	$y/x = 0.40$	0.40	0.40	0.40	0.40
87	—	—	—	2.5	—	—	0.43	0.41	0.42
88	—	—	—	3.5	—	—	0.36	0.34	0.39
89	—	—	—	5.0	—	—	0.38	0.37	0.38
90	15	20	20	0	0.64	0.70	0.73	0.80	0.84
91	—	—	—	2.5	0.51	0.54	0.60	0.65	0.65
92	—	—	—	3.5	—	0.46	0.50	0.57	0.61
93	—	—	—	5.0	—	0.40	0.44	0.49	0.52
94	20	20	20	0	0.85	0.92	0.97	1.02	1.02
95	—	—	—	2.5	0.62	0.71	0.78	0.84	0.84
96	—	—	—	3.5	0.53	0.63	0.69	0.75	0.75
97	—	—	—	5.0	0.69	0.70	0.71	0.72	0.72
98	—	—	—	10.0	0.60	0.61	0.60	0.61	0.61
99	20	20	10	0	0.77	0.82	0.89	0.94	1.01
100	—	—	—	5.0	—	0.52	0.50	0.51	0.51
101	—	—	—	10.0	—	—	0.50	0.50	0.48
102	20	10	20	0	0.68	0.76	0.75	0.82	0.82
103	—	—	—	5.0	0.42	0.61	0.62	0.67	0.71
104	—	—	—	10.0	—	0.61	0.63	0.62	0.64

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[1] Values of θ from 30 up.

Table XLV

Ac, 10; Cr, 20; KI, 20; Fe, 1.0; V, 700; *t*, 30.5° C

θ	Expt. 86 Ox 0; Cor. 0.66		Expt. 87 Ox 2.5; Cor. 0.70		Expt. 88 Ox 3.5; Cor. 0.70		Expt. 89 Ox 5.0; Cor. 0.7	
	As	x	As	x	As	x	As	x
0.25	1.30	0.65	—	—	—	—	—	—
0.50	1.65	0.83	—	—	—	—	—	—
1.0	2.00	1.00	1.05	0.49	1.00	0.54	0.93	0.50
2.0	—	—	1.55	0.74	1.40	0.83	1.40	0.75
4.0	—	—	2.10	1.00	1.95	1.00	1.90	1.00
16.0	2.00	1.00	2.10	1.00	1.95	1.00	1.90	1.00

Table XLV B θ = 16

Fe	Ox, 0 As	Ox, 2.5 As	Ox, 3.5 As	Ox, 5.0 As
0.2	0.40	0.40	0.40	0.40
0.4	0.86	0.80	0.85	0.80
0.6	1.20	1.25	1.20	1.20
0.8	1.65	1.65	1.65	1.65
1.0	2.00	2.10	1.95	1.90

Table XLVI

Ac, 15; Cr, 20; KI, 20; Fe, 1.0; V, 700; *t*, 30.5° C.

θ	Expt. 90 Ox 0; Cor. 0.70		Expt. 91 Ox 2.5; Cor. 0.70		Expt. 92 Ox 3.5; Cor. 0.70		Expt. 93 Ox 5.0; Cor. 0.65	
	As	x	As	x	As	x	As	x
0.25	2.30	0.71	—	—	—	—	—	—
0.50	2.80	0.80	1.10	0.43	1.02	0.44	0.90	0.45
1.0	3.10	0.85	1.85	0.65	1.42	0.57	1.35	0.61
2.0	3.85	0.96	2.50	0.83	2.44	0.85	2.20	0.90
4.0	4.20	1.00	3.25	1.00	3.05	1.00	2.60	1.00
8.0	4.20	1.00	3.25	1.00	3.05	1.00	2.60	1.00

Blanks:— Expt 90, θ = 8, Corr 0.20. Expt 92, θ = 8, As 0.35.
Expt 91, θ = 8, As 0.30. Expt 93, θ = 8, As 0.80.

Table XLVI B (θ = 8)

Fe	Ox, 0, As	Ox, 2.5 As	Ox, 3.5 As	Ox, 5.0 As
0.20	1.40	0.90	0.80	0.70
0.40	2.50	1.60	1.55	1.30
0.60	3.25	2.20	2.20	1.85
0.80	2.80	2.80	2.65	2.20
1.00	4.20	3.25	3.05	2.60

TABLE XLVII

Ac, 20; Cr, 20; KI, 20; Fe, 1.0; V, 700; *t*, 30.5° C

Corr: Expt 94, 0.75; Expt 95, 0.70; Expt 96, 0.72; Expt 97, 0.75; Ex 98, 0.82

θ	Expt. 94 Ox, 0		Expt. 95 Ox, 2.5		Expt. 96 Ox, 3.5		Expt. 97 Ox, 5.0		Expt. 98 Ox, 10.0	
	As	*x*	As	*x*	As	*x*	As	*x*	As	*x*
0.25	3.35	0.79	1.55	0.50	1.47	0.55	1.35	0.39	1.12	0.37
0.50	4.05	0.88	2.70	0.76	2.32	0.74	2.00	0.57	1.77	0.58
1.0	4.60	0.95	3.55	0.91	3.12	0.90	2.85	0.80	2.52	0.83
2.0	5.10	1.00	4.20	1.00	3.75	1.00	3.60	1.00	3.05	1.00
9.0	....	....	4.20	1.00	3.75	1.00	3.60	1.00	3.05	1.00
16.0	5.10	1.00	—	—	—	—	—	—	—	—
Blanks:	θ 16, Corr 0.2		θ 9, As 0.80		θ 9, As 1.05		θ 9, As 1.40		θ 4 9 16 As 0.80, 2.40, 5.00	

TABLE XLVII B

Fe	Ox, 0, As	Ox, 2.5 As	Ox, 3.5 As	Ox, 5.0 As	Ox, 10.0 As
0.20	1.70	1.30	1.15	0.80	0.60
0.40	2.75	2.20	2.10	1.50	1.20
0.60	3.85	3.10	2.75	2.30	1.85
0.80	4.60	3.60	3.25	2.90	2.45
1.00	5.10	4.20	3.75	3.60	3.75

TABLE XLVIII

Ac, 20; Cr, 20; KI, 10; Fe, 1.0; V, 700; *t*, 30.5° C

θ	Expt. 99 Ox, 0; Cor. 0.70		Expt. 100 Ox, 5.0; Cor. 0.75		Expt. 101 Ox, 10.0; Cor. 0.70	
	As	*x*	As	*x*	As	*x*
0.25	2.40	0.62	—	—	—	—
0.50	2.95	0.72	1.05	0.40	—	—
1.0	3.75	0.84	1.50	0.60	1.25	0.50
2.0	4.30	0.91	2.48	0.98	1.75	0.70
4.0	5.05	1.00	—	—	2.05	0.85
8.0	5.05	1.00	2.55	1.00	2.30	1.00
Blanks: θ = 8	Cor. 0.35		As, 0.85		As, 1.35	

TABLE XLVIII B ($\theta = 8$)

Fe	Ox, 0 As	Ox, 5.0 As	Ox, 10.0 As
0.20	1.60	0.50	0.30
0.40	2.75	1.05	0.80
0.60	3.75	1.55	1.30
0.80	4.35	2.05	1.80
1.00	5.05	2.55	2.30

TABLE XLIX

Ac, 20; Cr, 10; KI, 20; Fe, 1.0; V, 700; t, 30.5° C

θ	Expt. 102 Ox, 0; Cor. 0.75		Expt. 103 Ox, 5.0; Cor. 0.65		Expt. 104 Ox, 10.0; Cor. 0.82	
	As	x	As	x	As	x
0.25	2.55	0.76	0.80	0.38	—	—
0.50	3.25	0.88	1.35	0.44	1.22	0.40
1.0	3.70	0.95	2.10	0.67	1.87	0.59
2.0	4.10	1.00	2.75	0.82	2.67	0.82
4.0	—	—	3.50	0.99	3.20	1.00
8.0	4.15	1.00	3.65	1.00	3.20	1.00
Blanks: $\theta = 8$	Cor. 0.35		Cor. 0.20		As, 0.20	

TABLE XLIX B ($\theta = 8$)

Fe	Ox, 0 As	Ox, 5.0 As	Ox, 10.0 As
0.20	1.35	1.00	0.65
0.40	2.25	1.80	1.30
0.60	2.95	2.40	1.95
0.80	3.55	3.05	2.60
1.00	4.15	3.65	3.20

LIST OF EXPERIMENTS

Expt.	Table	Ac	Cr	KI	Ox	Fe	Temp.	Page	
49	36	10	20	20	5	1	0		Hydrochloric acid
50	36	20	20	20	5	1	0		"
51	37	10	20	20	0	1	0		0.88 g. K_2SO_4 added
52	37	10	20	20	0	1	0		0.5 g. NaCl added
53	37	10	20	20	0	0.5	0		"
54	37	10	20	20	0	1	0		"
55	37	10	20	20	0	0.5	0		1.0 g. "
56	37	10	20	20	0	0.5	0		"
57	37	10	20	20	0	1	0		1.0 g. KBr added
58	37	10	20	20	5	1	0		0.03 g. $KF.2H_2O$ added
59	37	10	20	20	5	1	0		0.1 g. "
60	37	10	20	20	0	1	0		0.5 g. "
61	37	10	20	20	0	1	0		1.0 g. "
62	38	10	20	(20)	0	1	0		
63–66	38	10	20	(20)	0	1	0		KF 1.0, 3.0, 5.0, 10.0
67	39	10	20	20	5	1	0		Agar-agar added
68	39	10	20	20	0	1	0		Albumen added
69	39	10	10	20	5&0	1	0		Dialyzed iron added
69	39	10	20	20	5&0	1	0		"
70–80	40	..	20	20	—	1	0		Various aged ox prods added
81–84	41	20	20	20	5&0	1	30.5		Various acid ox prods added
85	42	20	20	—	5	1	30.5		Correction for end point
—	43	—	20	—	5&0	1&0.5	0		Values of Induction factor
—	44	—	..	—	—	1	30.5		"
86–89	45	10	20	20	—	1	30.5		Ox 0, 2.5, 3.5, 5.0
90–93	46	15	20	20	—	1	30.5		"
94–98	47	20	20	20	—	1	30.5		Ox 0, 2.5, 3.5, 5.0, 10.0
99–101	48	20	20	10	—	1	30.5		Ox 0, 5.0, 10.0
102–4	49	20	10	20	—	1	30.5		"

The University of Toronto,
June, 1908.

NEW BOOKS

Spectrum Analysis. *By John Landauer. Authorised English edition by J Bishop Tingle. Second edition, rewritten. 15 × 23 cm; pp. 236. New York: John Wiley & Sons, 1907. Price: $3.00.*—"The general features of the former edition are retained in the present one. The measurements of spectra have been revised and brought up to date, the values being taken from Watts's 'Tables of Spectra.' This has involved a considerable amount of labor, and an increase in the size of the book, which has been reset entirely. The descripment of some of the older instruments has been eliminated in favor of a number of newer and superior forms, chiefly of American and English manufacture. It is hoped in this way the usefulness of the book has been increased without departing from its original plan. Although this edition is issued with Dr. Landauer's full consent, his health has, unfortunately, prevented his taking any active part in its preparation, consequently the writer takes the entire responsibility for any omissions or shortcomings which it may show. In judging it, regard should be had to its object. It does not pretend to be an exhaustive work on the subject, but merely an elementary guide to those who, with relatively little knowledge of physics, desire to understand something of the general scope and methods of spectrum analysis and to make practical use of the spectroscope; accordingly, special attention has been given to the cheaper forms of these instruments." *Wilder D. Bancroft*

Stereochemistry. *By A. W. Stewart. Edited by William Ramsay. 12 × 19 cm; pp. ix + 583. New York: Longmans, Green & Co., 1907. Price: $2.80.*—In the preface the author says in part:

"As it was obviously impracticable to mention every piece of work carried out within the last twenty years, a selection has been made of those cases which appear to throw most light upon the general lines along which research in stereochemistry is advancing at the present day, and the points so chosen have been treated in some detail. As some readers, however, may be interested in general principles only, and not in the details by which the current theories have been supported, it has been deemed expedient in the case of the chapter on Steric Hindrance to devote a section to a summary of the various researches which are described in detail in the other sections. The first and last sections of this chapter together form a connected whole, and the rest of it may be omitted by those who do not wish to become acquainted with the minutiae of the research work." ....

"Since the arrangement of atoms in space governs the physiological action of many drugs, it has been necessary to deal with the matter in some detail. In most works on stereochemistry, this part of the subject is treated in sections under the heads of the different classes of isomers; but, in the present volume, it seems better to consider the relations between stereochemistry and physiology in a more connected manner, and the question has therefore been dealt with in Appendix A."

The book is divided into two sections: stereoisomerism, and stereochemical problems into which isomerism does not enter. The first section is sub-divided into two parts: optical activity, and stereoisomerism without optical activity. Under optical activity the headings of the chapters are: the asymmetric carbon atom; inactive compounds; active compounds; the determination of configuration; the asymmetric carbon as a ring-member; two exceptional cases of optical activity; the quantitative relations between activity and the nature of the asymmetric carbon atom; other active elements; rotation.

Under stereoisomerism without optical activity the headings of the chapters are: cis-trans isomerism in cyclic compounds; geometrical isomerism in the ethylene series; geometrical isomerism in carbon-nitrogen compounds, stereoisomerism in nitrogen compounds; stereoisomerism in cobalt compounds; stereoisomerism in platinum compounds; stereoisomerism in chromium compounds.

In section two the headings are: the phenomena of steric hindrance; the relation between space formula and chemical properties; the effects of substitution upon the formation and stability of cyclic compounds; the configuration of optically inactive carbon compounds; the space formula of benzene. In the appendices we have the relations of stereochemistry to physiology and directions for the construction of stereochemical models.

The book is admirable, being well-planned and well-written. The reviewer would have liked to have seen the transmutation of tautomeric forms, p. 179, discussed a little more fully because that is a point on which the organic chemists are weak. *Wilder D. Bancroft*

Thermoelemente und Thermosäulen. *Ihre Herstellung und Anwendung. By Franz Peters. (Monographien über angewandte Elektrochemie. XXX. Band). 17 × 24 cm; pp. vi + 180. Halle: Wilhelm Knapp, 1908. Price: paper, 10 marks.*—The author gives a very welcome compilation of the facts in regard to thermocouples and thermopiles down to the end of 1906. He has included White's work on pyrometry; the Hoskins thermocouple and the Bristol thermocouple. It would have been well perhaps to have explained, p. 148, why the the electromotive force of a thermocouple increases when placed under a pressure of about 0.01 mm. The book does not pretend to be a treatise on the subject. It is essentially a compilation with the special reference to the patents. As such it will be useful. *Wilder D. Bancroft*

Die englischen elektrochemischen Patente. *By P. Ferchland. Auszüge aus den Patentschriften. (Monographien über angewandte Elektrochemie. XXIX. Band). 17 × 24 cm; pp. vii + 176. Halle: Wilhelm Knapp, 1907. Price: paper, 9 marks.*—Owing to the large number of English patents this volume contains only those relating to electrolysis. The patents are arranged chronologically and there is both a name and a subject index. In the preface the author remarks that "it is a fairly wide-spread opinion that technical men have only become impregnated with electrochemical ideas since the discovery of the osmotic theories." The gibe may be justifiable in Germany but in this country it seems rather pointless. *Wilder D. Bancroft*

Abhandlungen. *By Christian Doppler. (Ostwald's Klassiker der exakten Wissenschaften. No. 161). Herausgegeben von H. A. Lorentz. 12 × 19 cm; pp. 194. Price: bound, 3.60 marks. Leipzig: Wilhelm Engelmann, 1907.*—The volume contains eleven papers on optics and acoustics by Doppler and copious notes by H. A. Lorentz. *Wilder D. Bancroft*

INDIRECT ANALYSIS BY MEANS OF THE DILATOMETER: THE "LOWER HYDRATE" OF SODIUM ACETATE

BY W. LASH MILLER

In order to avoid the difficulties which sometimes attend the removal of mother-liquor from the solid products of a reaction,[1] various "indirect" methods of analysis have been devised for determining the composition of the latter.[2]

The method employed in the present paper is different in principle from those hitherto suggested; while less general in its application than some of them, it is perhaps the most convenient in the large group of cases to which it is applicable.

The behavior of crystallized sodium acetate, $C_2H_3O_2Na.3H_2O$, on heating, was first described by Jeannel[3], who found that it begins to melt at 58° C, becomes completely liquid at 75°, and boils at 123°.

When he let the melted salt cool gradually in the air, it crystallized at 58° in prismatic needles, the temperature keeping constant at that point during the crystallization;[4] but if the solution was protected from "germs" it solidified to a white translucent mass of large shiny leaflets covered with a little liquid.

These leaflets were deliquescent in air, in which the prismatic salt dried out, and were easily converted into the latter by bringing into dry air, or by touching with a glass rod,

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[1] Bancroft: Jour. Phys. Chem., 6, 178 (1902); Lash Miller and Kenrick: Ibid, 7, 259 (1903).

[2] v. Bijlert: Zeit. phys. Chem., 8, 343 (1891); Schreinemakers: Ibid., 11, 81 (1893); Kentner: Ibid., 39, 658 (1902); Bancroft: Jour. Phys. Chem., 6, 178 (1902); 9, 558 (1905); Browne: Ibid., 6, 287 (1902).

[3] Comptes rendus, 62, 834 (1866).

[4] Jeannel suggested the use of melted sodium acetate for testing and standardizing thermometers; a note on the suitability of the salt for this purpose will shortly be published.

or with a crystal of "ordinary" sodium acetate—dehydrated sodium acetate had no effect.[1]

Although the supersaturated solutions of sodium acetate have been studied by a large number of authors, among them Reischauer,[2] Gernez,[3] Böttger,[4] Thomson,[5] and Baumhauer,[6] the composition of the leaflets described by Jeannel has not yet been ascertained with certainty. They are commonly referred to in the literature as "a lower hydrate,"[7] and Gernez,[8] though without quoting his authority, gives them the formula $2C_2H_3O_2Na.3H_2O$; but the only analyses of which I have been able to find any account are due to Zettnow.[9]

This chemist melted the commercial acetate in a flask, boiled the liquid, closed the mouth of the flask with cotton wool, and drained the crystals deposited on cooling, by tilting the flask. When the cotton was removed, the (supersaturated) mother-liquor solidified, breaking the flask; the upper layer of crystals was then removed and analyzed, with the following results (in Expts. 3 and 4 the melting was repeated):

TABLE I

Expt.	Water Percent	Formula
1	35.66	$C_2H_3O_2Na$ 2.52 H_2O
–	35.33	" 2.49 "
2	21.33	" 1.24 "
3	18.14	" 1.03 "
–	21.05	" 1.20 "
4	20.04	" 1.14 "
5	32.6	" 2.20 "
6	33.3	" 2.27 "

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[1] Berthelot: Comptes rendus, 77, 975 (1873).

[2] Liebig's Ann., 115, 116 (1860).

[3] Jahresbericht, 1865, 75.

[4] Jahresbericht, 1867, 390.

[5] Jour. Chem. Soc., 35, 196 (1879).

[6] Jour. prakt. Chem., 104, 449 (1868).

[7] Ostwald: Lehrbuch II, (2) page 770 (1902).

[8] Comptes rendus, 84, 1389 (1877).

[9] Pogg. Ann., 142, 306 (1871).

The author regards his experiments as establishing the existence of the hydrates $C_2H_3O_2Na.H_2O$, $2C_2H_3O_2Na.5H_2O$, and $2C_2H_3O_2Na.9H_2O$; in the absence of proof that his crystals were free from mother-liquor, however, much weight cannot be attached to these results. The formate and valerate of sodium crystallize with one mol of water, but Thomson's[1] observations that these salts cause no formation of crystals in supersaturated solutions of sodium acetate speaks against the existence of a hydrate $C_2H_3O_2Na.H_2O$.

On repeating Jeannel's experiments it was at once apparent that the "partial melting" at 58° C consists in the complete disappearance of the crystals of trihydrate, and the formation of a solution and of crystals of a new salt (leaflets); a few more experiments, carried out after the manner of Zettnow's, showed that both solution and leaflets, like the trihydrate from which they were formed, were slightly alkaline to litmus. From this observation (which was subsequently confirmed with the crystals separated by the centrifugal apparatus described by Mr. Green)[2] it follows that the leaflets consist of a neutral acetate of sodium, hydrated or anhydrous; as, if they had been formed of an acid or basic acetate, either the crystals themselves or the mother-liquor must have had an acid reaction.

The "partial melting point" of the trihydrate, then, must be considered as the temperature at which the reaction

$$C_2H_3O_2Na.3H_2O = C_2H_3O_2Na.xH_2O + \text{Solution} \ldots \quad (i)$$

is in equilibrium; in other words, it is a transition point in a two-component system, and the following

Considerations based on the phase rule

lead to a method of determining the composition of the crystals in question without removing them from the mother-liquor.

As the existence of equilibrium in heterogeneous sys-

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[1] Loc. cit., page 203.

[2] Jour. Phys. Chem., 12, 655 (1908).

tems is not dependent on the quantities of the various phases present, addition of $C_2H_3O_2Na.xH_2O$ in any quantity would cause no change in the temperature of "melting," in the composition of the solution, or in the amount of trihydrate present. Addition of a third hydrate, however, or of the anhydride (supposing x different from 0) renders a new reaction possible, *viz.*, reaction (*ii*), between trihydrate, x-hydrate, and third hydrate (or anhydride); and, as it is very unlikely that both reactions *i* and *ii* will be in equilibrium at the same temperature,[1] it is fair to assume that reaction *ii* will proceed until either the new hydrate or the trihydrate is completely used up.

If y be taken to represent the number of mols of anhydride mixed with A mols of trihydrate, reaction *ii* may be represented by the following chemical equation:

$$\frac{xy}{3-x}(C_2H_3O_2Na.3H_2O) + y(C_2H_3O_2Na) = \frac{xy}{3-x}(C_2H_3O_2Na.xH_2O) \qquad (ii)$$

which shows that $xy/(3-x)$ mols of the trihydrate would disappear, leaving only $A-xy/(3-x)$ mols to enter into reaction *i*.

A determination of the residual trihydrate, therefore, together with the known values of A and y, is sufficient to determine x, that is, the composition of the crystals formed by melting the trihydrate at 58° C.

The easiest way to determine the amount of trihydrate in a mixture of trihydrate and x-hydrate is to heat to 58° and measure the change of volume which accompanies the "melting." This is obviously proportional to the amount of trihydrate present; by means of a blank experiment, in which the dilatometer is filled with a known quantity of the pure trihydrate, the weight of that salt corresponding to one division of the dilatometer scale may be ascertained.

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[1] The statement of the phase rule, that in a two-component system at arbitrary pressure not more than three phases can exist in equilibrium, is only another way of putting this.

Dilatometer measurements

To facilitate the introduction of weighed amounts of salt into the dilatometer, the bulb of the latter was replaced by a cylindrical vessel closed by a perforated cork with capillary through which the (dried and air-free) coal oil was sucked into the instrument; contrary to expectation, there was no trouble due to swelling of the cork when the whole was immersed in the water bath.

Two sets of measurements were carried out: the first with 4.040 grams of the pure trihydrate, and the second with 3.350 grams of a mixture prepared by grinding trihydrate and anhydride together, heating for some time above 60°, cooling, and powdering again. The amount of water in this mixture was determined by heating to 120° until the weight was constant:

Weight before heating	1.7156 g.
Weight after heating	1.4460

Table II

4.040 g. trihydrate			3.350 g. mixture		
Interval Hrs. min.	Temp.	Dilatr. div'ns	Interval Hrs. min.	Temp.	Dilatr. div'ns
— 30	56.6° C	47.0	— 7	57.0° C	123.0
— 27	57.0	48.0	— 7	57.5	126.0
— 11	57.5	51.0	— 5	58.0	131.5
— 8	58.0	53.0		58.5	143.0
3 12	58.5	56.8		Heated to 75°	
17 0	59.0	227.0	1 4	59.5	188.0
1 10	59.35	229.0		58.8	187.5
1 5	58.7	228.0			
	56.3	220.0	(Interp)	58.0	187.0 melted
				58.0	131.5 solid
(Interp)	58.0	224.5 melted			
	58.0	53.0 solid		Expansion	55.5
	Expansion	171.5			

Assuming that the melting takes place at 58° on the thermometer employed, the first experiment shows that the expansion per gram of trihydrate melted is 42.44 divisions of the dilatometer scale. The expansion of the mixture, 55.5 divisions, corresponds to 1.308 grams of trihydrate or 0.009616 mols.

Thus $A - xy/(3-x) = 0.009616$. The values of A and y, calculated from the weight and composition of the mixture, are 0.009750 and 0.02346, respectively; from which it follows that $x = 0.017$, or that the composition of the "x-hydrate" is $C_2H_3O_2Na$. $0.017H_2O$.

The reliability of this result obviously depends on the accuracy of the dilatometer measurements. The error of each of the expansions measured is probably at least one scale division, but certainly less than five divisions; while even if 5 divisions be added to the expansion of the trihydrate and 5 be subtracted from that of the mixture—the most unfavorable combination—the value of x rises only to 0.16.

The measurements therefore prove conclusively that the crystals deposited by the trihydrate on "melting" consist of anhydrous sodium acetate.

The University of Toronto,
June 1908.[1]

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[1] Read before the American Chemical Society at the Buffalo Meeting September 1905, under the title "A new use for the Dilatometer"

THE "MELTING-POINT" OF HYDRATED SODIUM ACETATE: SOLUBILITY CURVES

BY W. F. GREEN

In the preceding paper Professor Lash Miller has shown that the composition of the crystals formed by "melting" sodium acetate trihydrate may be ascertained by means of dilatometer measurements, without isolating the crystals from the solution; the following experiments were undertaken to obtain evidence in confirmation of the result there arrived at—*viz*: that "Jeannel's leaflets" are anhydrous sodium acetate.

Isolation of the leaflets

The first attempts were made by centrifuging the mixture of leaflets and (supersaturated) mother-liquor;[1] the crystals left behind all proved to contain water (Table I,*a*), in one case more than the least found by Zettnow. That this water was due to residual solution—partly, at all events—was shown by dissolving a little rosaniline acetate in the melt; after cooling and centrifuging, the inner layers of crystals were quite colorless; but those next the cork were strongly tinged with red, showing how difficult it is to remove the viscous mother-liquor, and readily explaining the large percentage of water left in Zettnow's preparations, which were dried merely by draining in the cold.

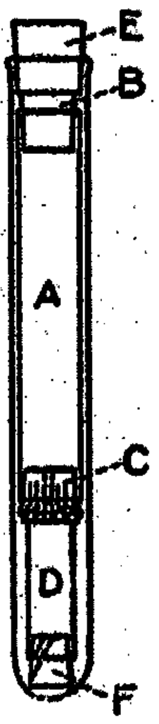

Fig. 1

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[1] The apparatus employed is represented in Fig. 1, it was designed to prevent access of dust to the supersaturated solution. The inner tube *A* was filled with the trihydrate and closed at the ends with the corks *b* and *c*, of which *c* was perforated and covered with hardened filter paper. The whole was then inserted in the outer tube, which contained a short piece of thick glass tubing *D*, provided with a perforated rubber stopper, the outer tube was then corked, *E*, and left standing, *E* down, in a steam bath until the acetate was melted. After cooling, the apparatus was placed in the centrifuge, *D* outwards, and the mother-liquor separated from the crystals which remained inside *A*.

A hundred grams of the hydrated acetate was then melted in a cylindrical tap funnel, the mouth of which was closed with a plug of cotton wool. After cooling to 15° the stem was filled with water to prevent the entrance of "germs," and connected with a vacuum pump; in this way most of the liquid was removed. The crystals were then drained for some hours in a steam bath at 95° the tap of the funnel being left open, and finally as much as possible of the remaining mother liquor was pumped off hot. On cooling, the upper part of the funnel was found to be filled with a white crust, and the bottom with moist crystals (Table I,*c*), but the crystals in the middle of the funnel retained their form and were transparent, bright and sharp, showing conclusively that they had suffered no change by being heated to 95°, but were identical with the "leaflets" deposited at 15°. Analysis showed them to be anhydrous (Table I,*b*).

Prepared in this manner, the crystals form either thin plates or long thin needles;[1] their melting-point[2] was identical with that of a sample of anhydrous acetate prepared by dehydrating the trihydrate and melting the salt so obtained; both melted at 322° to 324° uncorr.; Schaffgotsch[3] gives 319° as the melting-point of $C_2H_3O_2Na$.

Solubility determinations

Solubility of the Anhydrous Salt.—For temperatures above 58° the determinations were made in an open test-tube of 100 cc capacity, in which the crystals prepared as just described were stirred with water by a strip of window glass bent into a spiral and fused to a glass rod. The apparatus stood in a thermostat, except for the determination at 123° when the contents of the tube were boiled over a Bunsen flame.

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[1] According to Haushoffer (Zeit. f. Krystallogr., 4, 572 (1880)) sodium acetate crystallizes from alcoholic solution in spear-formed needles and in plates.

[2] Determined in a capillary tube, with high-temperature mercury thermometer, in a bath of anthracene which had recently been distilled to make it transparent.

[3] Pogg. Ann., 102, 293 (1857).

A warmed glass tube, constricted about ¼ inch above its lower end which was filled with a loose plug of absorbent cotton, served to remove a portion of the solution for analysis; the lower end of the tube was quickly cut off with a pair of scissors, and the solution blown out into a weighed crucible, which was immediately covered and weighed again. The water was driven off without spirting by heating for some hours in a steam bath at 95° and then to constant weight at 120°. The results are given in grams of anhydrous salt per 100 g water, and are in most cases the means of accordant determinations.

At temperatures below 58°, where the solutions are supersaturated with respect to the trihydrate, the combination of tap funnel *A*, adapter *B*, and vial *C* shown in Fig. 2 was employed. A quantity of trihydrate was melted in the funnel, the apparatus set together and tied to the piece of board weighted at *G*, and was rocked about the axis *H* in a thermostat over night. A partial vacuum was then created in the adapter by means of a rubber tube attached to *F*, the tap *D* was opened a little and the vial filled. The tap was then closed and the whole removed from the thermostat; the stopper *E* and vial removed, part of the solution quickly poured into a crucible and treated as described. After washing and drying vial and adapter, the apparatus was ready for another determination.

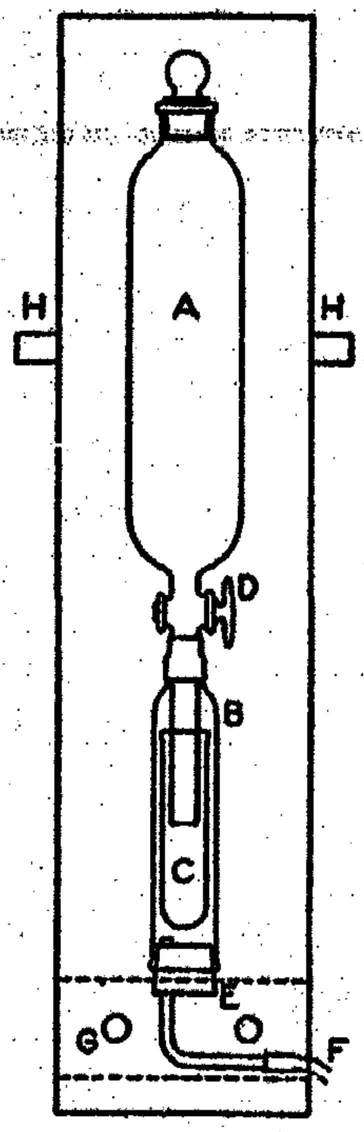

Fig. 2

Solubility of the Trihydrate.—These measurements were made in the open vessel used for the anhydrous salt above 58°; the results are expressed in the same units as before, *viz.*: grams of anhydrous salt to 100 grams of water in the solution. Four numbers are taken from Schiavon[1] and one from Guthrie.[2]

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[1] Gazz. Chim. Ital., 32, 532 (1903).

[2] Phil. Mag. [5], 2, 215 (1876).

Table III gives the solubilities for every 10°, obtained by graphic interpolation from the figures of Table II. The data for the freezing-point and boiling-point curves are taken from tables by Legrand[1] and Guthrie,[2] respectively. The four curves in Fig. 3 give the compositions of solutions saturated with anhydride, trihydrate, ice, and steam at atmospheric pressure, respectively.

TABLE I

Expt.	Water Percent	Mols H_2O to one mol $C_2H_3O_2Na$	
	18.14	1.03	Zettnow's driest
a	33.0	2.24	Centrifuged
	5.4	0.3	Centrifuged
b	0.6	0.03	Drained hot
	0.37	0.016	Drained hot
	0.36	0.016	Drained hot
c	4.0	0.22	Bottom of funnel

TABLE II

Anhydrous				Trihydrate		
0°	119	72°.5	149	0°	36.2	Guthrie
25	125	83	154.3	9	40	Schiavon
34.8	129	83.5	154.3	13	43.5	Schiavon
43	131	100	170	37	61.0	Schiavon
50	133.5	123	193	41	68.0	Schiavon
61	140.5	—	—	51.5	87.5	Green
—	—	—	—	55.5	102	Green.

TABLE III

Temp..........	−18°	−10°	0°	10°	20°	30°	40°	50°	58°
Ice............	30.4	19.0	0	—	—	—	—	—	—
Hydrate........	30.4	33.0	36.3	40.8	46.5	54.5	65.5	83	138
Anhydrous.....	—	—	119	121	123.5	126	129.5	134	138

Temp..........	60°	70°	80°	90°	100°	110°	120°	123°
Anhydrous.....	139.5	146	153	161	170	180	191	193
Steam.........	—	—	—	—	0	69	156	193

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[1] Lieb. Ann., 17, 36 (1836); see also Gerlach: Zeit. anal. Chem., 26, 455 (1887).

[2] Loc. cit. See also Rüdorff: Pogg. Ann., 145, 616 (1872).

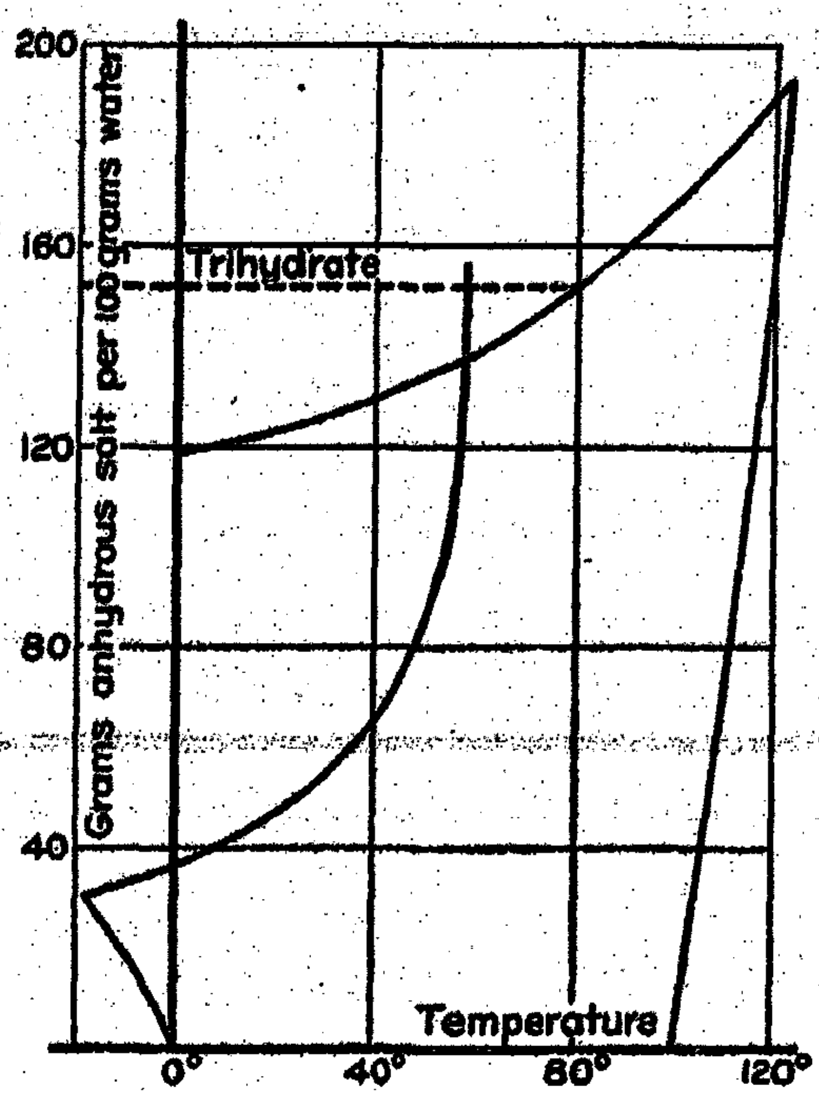

Fig. 3

Summary

The crystals deposited from supersaturated solutions of sodium acetate trihydrate have been isolated and analyzed; in confirmation of the results obtained by dilatometer measurements they consist of anhydrous sodium acetate. The crystalline form and the melting-point of the salt so obtained are those of ordinary anhydrous sodium acetate.

The solubility of the anhydrous salt has been determined from 0° to 123°—the boiling-point of the saturated solution; and that of the trihydrate from the cryohydratic point (Guthrie) to its "melting-point."

The "melting-point" of the trihydrate is a transition point, at which the reaction

$$C_2H_3O_2Na.3H_2O = 0.092\ C_2H_3O_2Na + \text{Sol'n}\ (0.908\ C_2H_3O_2Na + 3H_2O)$$

is in equilibrium. As noted by Jeannel, the "melting" at 58° is incomplete; the lowest temperature at which a clear solution can be obtained is obviously that at which the solution saturated with the anhydride has the same composition as the crystals of the trihydrate, *viz.*: 152 grams salt to 100 grams water. This is the case at 79°, where the dotted line corresponding to the composition of the trihydrate in Fig. 3 cuts the solubility curve of the anhydrous salt; Jeannel gives 75°, Zettnow 77° to 78°.

The "true melting-point," at which trihydrate is in equilibrium with a solution of its own composition, would be given by the intersection of the same dotted line with the solubility curve, produced, of the trihydrate. This temperature would be very little higher than that of the transition point, as at the true melting-point the tangent to the solubility curve must be perpendicular.

These measurements were carried out under the direction of Prof. W. Lash Miller in the chemical laboratory of the University of Toronto in the spring of 1903.

The University of Toronto,
June, 1908.

A SIMPLE METHOD OF DETERMINING VAPOR-DENSITIES[1]

BY PHILIP BLACKMAN.

Part I

Apparatus

The apparatus is of glass and consists of a stout, long bulb, having a tight-fitting stopper at one end, and at the opposite end, a long capillary-tube with a tap at its extremity. By means of a split cork, it can be fixed in a flask fitted with a condenser. The volume of the bulb (*i. e.*, when the stopper is in position) is determined once for always, and the capillary-tube has marked along it, a linear scale (cms divided into mm). Two threads of mercury are introduced, one to close the tap, the other near the bulb; the air-space between the two threads will serve as an air-manometer (a pressure-gauge). A weighed quantity of the substance to be experimented on is introduced in a small stoppered tube, a little mercury (1 cc) poured in, the stopper fixed and bound firmly to the neck with wire, the whole fixed in the flask, and then heated in the vapor of some liquid, boiling above the temperature at which the substance vaporizes. It will be observed that solid substances, as well as liquids, capable of existing in the state of vapor, can be dealt with

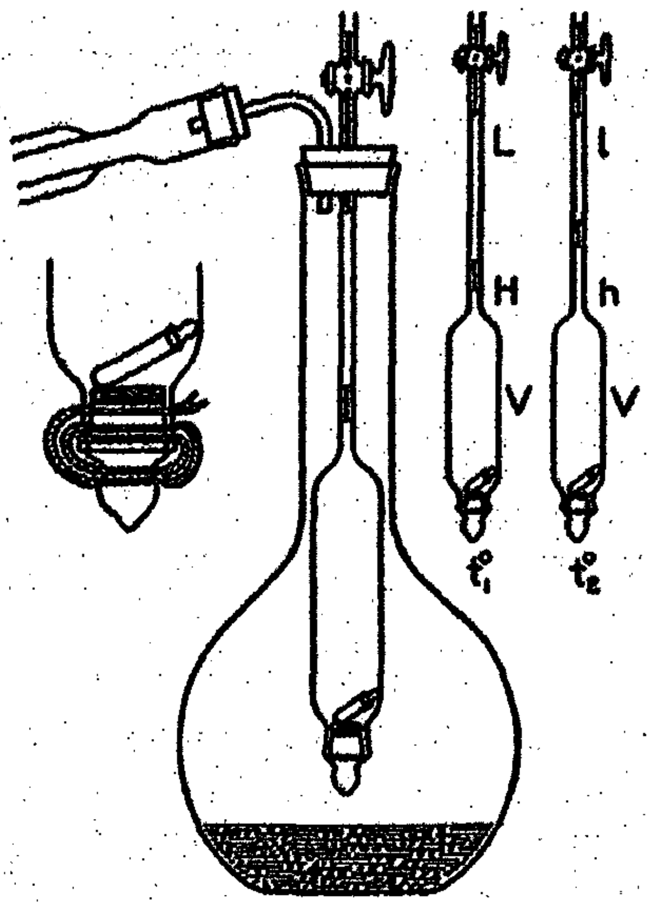

Fig. 1

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[1] Read before a meeting of the Chemical Society, London, January 16th, 1908. Compare Chemical News, 97, 102 (1908).

by this method. The final reading is taken when the air in the gauge remains constant in volume. When the apparatus has cooled down, it may be heated to some other suitable temperature and a fresh reading taken; this process may be repeated any number of times, each giving an independent result.

Theory

Let p = the atmospheric pressure (mm) and $t_1°$ = the temperature of the air, when the substance, of weight w, was introduced;

V = the volume of the bulb;

L, l = the lengths of the air-gauge at $t_1°$, and $t_2°$ respectively;

$H h$, = the respective volumes of the space in the capillary between the bulb and the movable mercury thread, at $t_1°$ and $t_2°$;

$t_2°$ = the temperature of the heating vapor.

If a = the area of the cross section of the bore of the capillary-tubing, we have

(1) the final total pressure $= \dfrac{pLa(273 + t_2)}{la(273 + t_1)}$;

(2) the pressure of the air in the bulb

$$= P(V + H)(273 + t_2)/(V + h)(273 + t_1);$$

(3) the pressure of the vapor, therefore,

$$= (1) - (2) = \pi = \frac{p(273 + t_2)}{(273 + t_1)}\left(\frac{L}{l} - \frac{V + H}{V + h}\right).$$

The volume of the vapor at 0° and 760 mm = $273\,\pi(V + h)/760(273 + t_2)$, and its density is = w divided by this last expression $= \dfrac{760\,w(273 + t_1)}{273p(V + h)\left(\dfrac{L}{l} - \dfrac{V + H}{V + h}\right)}$.

When compared with the vapor-density of hydrogen at 0° and 760 mm (assuming that 1 gram of hydrogen occupies 11160 cc) the formula becomes

$$\frac{31068\,w\,(273 + t_1)}{p(V + h)\left(\dfrac{L}{l} - \dfrac{V + H}{V + h}\right)}.$$

For ordinary purposes, however, seeing that h and H are generally very small compared with V, sufficiently accurate results will be obtained by neglecting h and H and using the formula

$$\frac{31068\,wl(273+t_1)}{pV(L-l)}.$$

Indeed, the author found in practice that the results as calculated by means of this formula are scarcely 0.5 percent greater than if calculated by the preceding more complicated formula.

Precautions

(1) If water be used as the heating liquid, no condenser is required.

(2) It is most difficult to keep the stopper perfectly air-tight during an experiment. A small quantity (1 cc should be found quite sufficient) of mercury—allowance for its volume must be made in the calculations—is introduced into the bulb before the substance is introduced. The mercury will settle over the stopper and close effectively any space between it and the neck.

(3) When the gaseous pressure within the bulb is considerable, the mercury thread may be forced out round the tap. To avoid this occurring, the tap should be fastened firmly with wire to the capillary.

(4) In very accurate work, allowance will have to be made for the volumes of the tube and the contained substance.

(5) Generally, when a substance of unknown molecular weight is experimented on, not more than 0.1 gram of it, per 50 cc of bulb should be employed.

(6) No substance should be experimented on which is likely to affect the mercury.

(7) The thread of mercury closing the tap must be long enough to reach below the level of the outlet for the heating vapor. This will necessitate a fairly long thread, and allowance for its expansion, if it be considerable, may be made thus:

when the mercury has ceased to expand, the tap is very cautiously opened; the internal pressure will force the mercury outwards, and when the end of the thread has reached its initial position, the tap is turned off, after which the reading for l is taken.

(8) The other thread need not be much more than 1.0 cm in length and no allowance for its expansion will then be needed.

(9) If the apparatus be totally suspended from the cork within the vessel, both mercury threads may then be short and no allowance for expansion will then have to be made; however, there is some risk of the tap breaking when the apparatus is being heated.

(10) Before use, the apparatus should be thoroughly cleaned and dried, and a current of air drawn through it to remove any vapors.

(11) After the substance has been introduced into the bulb, the stopper must be immediately fixed and bound firmly with thin wire to the neck to prevent its moving while it is being fastened on, aided by pliers, with soft copper wire (1/16 to 1/20 inch in diameter) to the neck. Care must be taken to wind the wire in the same direction, else it will be untwisted in one place while it is being tightened in another. During this operation, the apparatus should be held bulb downwards.

(12) The length of the air-thread in the manometer will be slightly lengthened, due to the weight of the movable mercury thread. The correct length l_c required is given by $\frac{L}{l} = \frac{L}{l_c} - \frac{M(273 + t_1)}{p(273 + t_2)}$ in which M is the length (mm) of the movable mercury thread.

(13) Clean, dry mercury only should be used.

Advantages

The apparatus is simple in construction and is, therefore, cheap and easily manipulated, and is capable of giving good results in a short time (30–45 minutes).

Results

The heating liquid employed was, in all the experiments, water, and no condenser was used. No determination failed to give a good result, when the stopper was well closed (as indicated by no expulsion of mercury). Allowance in every case was made for the volume of the weighing tube and the contained substance.

Substance	*w* gram	l_c mm	$t_1°$	*p* mm	V cc	$L - l_c$ mm	Vapor density	
							Found	Theory
C_2H_5Br	0.073	85	10.5	750	27.3	48	55.25	54.48
"	0.279	36	15.5	750	26.0	88	52.26	54.48
C_2H_5I	0.159	59	14.5	747	29.3	54	70.64	77.92
" (purer)	0.157	63	16.5	750	29.2	55	72.54	77.92
$CH_3.CO_2C_2H_5$	0.054	86	14.0	747	29.3	41	45.97	44.00
$CH_3.CO.CH_3$	0.070	52	17.0	741	29.2	55	27.45	29.00
"	0.063	71	16.5	740	29.2	64	28.68	29.00
"	0.060	52	16.5	741	29.2	49	26.22	29.00
$CH_3.CN$	0.016	100	15.5	743	29.2	31	20.96	20.52
"	0.020	90	14.0	743	29.2	33	22.25	20.52
CH_3I	0.126	73	16.0	749	29.2	52	72.15	70.93
"	0.111	80	17.0	750	29.2	52	72.60	70.93
C_6H_6	0.009	114	17.0	750	29.2	11	37.99	39.00
"	0.036	90	17.0	750	29.2	36	36.88	39.00
"	0.017	99	17.0	746	29.2	18	38.42	39.00
$CH_3.OH$	0.014	85	16.0	750	29.2	30	16.14	16.00
"	0.020	80	16.0	750	29.2	40	16.29	16.00
$(C_2H_5)_2O$	0.018	105	17.0	748	29.2	20	38.75	37.00
"	0.020	105	16.5	748	29.2	22	39.09	37.00
"	0.014	105	15.5	750	29.4	16	37.07	37.00
$C_2H_5.OH$	0.018	86	16.5	750	29.4	26	24.07	23.00
"	0.021	90	17.0	750	29.2	33	23.39	23.00
CS_2	0.021	104	16.0	745	29.2	23	38.81	38.06
"	0.030	97	17.0	746	29.2	30	39.82	38.06
"	0.061	80	16.5	746	29.2	50	40.00	38.06
$CHCl_3$	0.021	112	15.5	759	29.2	16	58.66	59.67
"	0.024	111	15.5	759	29.2	18	59.13	59.67
CCl_4	0.023	112	16.0	759	29.3	13	78.71	76.90
"	0.024	115	16.0	759	29.2	14	78.49	76.90

I must tender my thanks to R. Blair, Esq., Executive Officer of the L. C. C., and to the authorities of the Hackney

Technical Institute, N. E., for the facilities granted to me to carry out the research (London).

Part II[1]

Apparatus

The following modified form of the apparatus is one of the best means for determining vapor-densities, considering its simplicity, and the ease and accuracy with which results can be obtained. Its advantages over the first form of the apparatus are that (1) it contains neither tap nor joints, (2) it has no stopper; (3) a split cork for fixing is not required; (4) no mercury is necessary for sealing and (5) increased accuracy is obtained due to increase in V, L and l, and (if desired) w. The apparatus consists of two parts, a capillary-tube and a bulb.

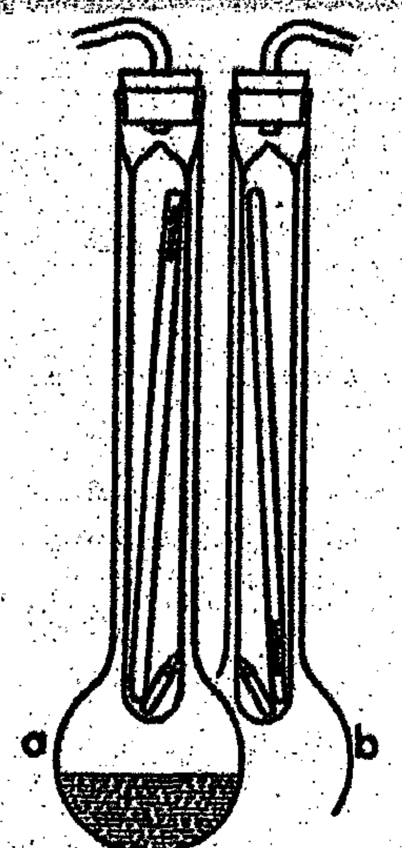

Fig. 2

The capillary-tube may be either straight or U-shaped; in the latter case, greater values for L, L_e, and l are obtained. One end is sealed, and a scale of cms (divided into mm) is marked along it. A short thread of mercury is introduced into the open end, and the air-space of length L thus enclosed, serves as the air-manometer.

The bulb consists of a clean, dry, glass tube, sealed at one end; through the open end, the small stoppered weighing tube with its contained weighed quantity of the substance to be experimented upon is dropped in, the manometer is put in and the open end of the tube is sealed up. When the glass has again cooled down to t_1°, the length L_e of the air-thread in the manometer is observed (see Precaution (7) further on). The bulb is now suspended from the cork within a flask, or better, within

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[1] Compare Zeit. phys. Chem., 63, 48, 381 (1908).

a Victor-Meyer's-heating-jacket, and heated in the vapor of some suitable liquid.

When the reading for l has been made, the bulb is removed and left to cool; a small portion of the glass at one end of the bulb is cut off; and (neither the manometer nor the weighing-tube is to be removed) the volume V of the bulb is determined by dropping in water from a burette.

Theory

The formula to be applied when calculating the vapor-density is either

$$\frac{31068\, wl_c L_{tc}(273 + t_1)}{pL(V + h)\left(L_{tc} - l_c \cdot \frac{V + H}{V + h}\right)},$$

or preferably (because less complicated and giving almost equally correct results)

$$\frac{31068\, wl_c L_{tc}(273 + t_1)}{pL_t V(L_{tc} - l_c)},$$

Precautions

(1) To introduce the mercury, the capillary-tube is warmed by passing over a Bunsen-flame, the open end placed in mercury, and a thread allowed to run in as the glass cools; L_t is measured when the manometer has cooled to the room-temperature, t_1°.

(2) To clean the capillary-tube, shake it sharply to eject the mercury; introduce a little, pure, suitable solvent and shake it out; finally dry the tube. If it becomes too dirty to be cleaned thus, the sealed end is cut off, the bore thoroughly cleaned and dried and one end again sealed. If the bore be not absolutely clean and dry, then any impurity in it will, when the apparatus is being heated, vaporize and will thus cause not only error in l but also the expulsion of the mercury from the bore. The mercury also must be quite pure, otherwise, on the application of heat, it will break up into a number of drops and be expelled from the bore.

(3) The temperature, $t_2°$, of the heating medium should be considerably higher than that of the substance experimented on, as the latter (until completely vaporized) has to vaporize under continually increasing pressure.

(4) To suspend the bulb, some wire or string is wound round it, the ends being passed round the cork.

(5) The manometer can be placed with either (*a*) the open end, or (*b*) the closed end, towards the top. It should be possible to read L, L_c, and l accurately to half a mm.

(6) Allowance must be made for, (*a*) the compression, or (*b*) the extension (see (*a*) and (*b*) of Precaution (5)) of the air in the manometer due to the weight of the mercury-thread [(1) the pressure with the manometer horizontal = $\frac{pL(273+t_2)}{l_c(273+t_1)}$; (2) the pressure with the manometer vertical = $\frac{pL(273+t_2)}{l(273+t_1)}$; and, if M is the length measured in mm of the mercury-thread, (1) ± M = (2)], the correct length l_c is given by the equation

$$\frac{1}{l}=\frac{1}{l_c}\pm\frac{M(273+t_1)}{pL(273+t_2)},$$

[+ in case (*a*), — in case (*b*)]. The correction is especially necessary when L_c and l do not differ greatly in the value, as the error for l_c in such cases may amount to as much as $\mp 3L_c/100$. The readings for L and L_c are taken with the manometer held horizontally and no such correction is needed.

(7) After the tube has been sealed and left to cool to $t_1°$, the internal pressure has changed (it always becomes less than p). The change in the internal pressure must be allowed for by observing the alteration that has been produced in L; thus, if L (before sealing the bulb) changes to L_c (after the bulb has been sealed) the pressure alters to pL/L_c, and the formula must be written (by putting pL/L_c for p and L_c for L)

$$\frac{31068\,wl_cL_c(273+t_1)}{pL(V+h)\left(L_c-l_c\frac{V+H}{V+h}\right)}.$$

(8) When working with an extremely volatile substance, it is perhaps better to seal it up in a very thin glass tube (whose weight is known and subtracted from the combined weight of the substance and tube); this can be very easily broken (after the bulb has been sealed and L_c measured) by shaking the bulb to cause the manometer to strike against it, thus liberating the contained substance. This method of weighing should certainly be used when experiments are carried out upon very unstable substances.

Results

The heating medium was steam (t_2 = 100°), and a condenser was not employed.

Substance	w gram	l_c mm	t_1 °C	p mm	V cc	L mm	L_c mm	Vapor-density	
								Found	Theory
CH_3I	0.7562	156	16.5	759	94.9	363.5	364	70.78	70.93
C_2H_5I	0.2120	236	17.5	755	78.2	341	343	71.73	77.92
C_2H_5Br	0.3721	143	16.5	763	70.5	317	318	51.31	54.48
$CH_3.OH$	0.1639	162	16.0	761	116.7	324.5	326.5	15.73	16.00
$C_2H_5.OH$	0.1814	193.5	16.5	757	88.5	388.5	390	23.89	23.00
$(C_2H_5)_2O$	0.2810	155	16.0	756	88.2	314.5	316	36.52	37.00
$CH_3.CO.OC_2H_5$	0.1351	257.5	15.0	754	73.2	379	380.5	45.73	44.00
$(CH_3)_2CO$	0.1978	177	17.0	749	91.8	334	337.5	28.60	29.00
$CH_3.CN$	0.2013	160	16.5	761	102.3	324.5	325.5	22.42	20.52
CS_2	0.4265	146	16.5	765	99.5	321.5	322.5	41.63	38.08
CCl_4	0.2448	232	16.0	765	68.4	363.5	365	75.15	76.90
$CHCl_3$	0.2176	271.5	16.5	766	90.2	393.5	395	62.01	59.67
C_6H_6	0.3230	166	17.0	755	97.5	336	337	38.35	39.00

Part III[1]

If every precaution be taken to determine the various quantities correctly, and making all allowances in the calculations—see Precautions (6) and (7) in Part II—the method may be used for determining quickly and accurately, the constituents by weight of a mixture of two substances, or to determine the quantity of an impurity in a substance.

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[1] Compare Zeit. phys. Chem., 63, 52 (1908).

Let w_1, w_2 be the required weights of the two substances whose vapor-densities are d_1, d_2 respectively. Let ϕ be the pressure due to the mixture of vapors at t_2°, then

$$\frac{11160 \times 760}{273}\left(\frac{w_1}{d_1}+\frac{w_2}{d_2}\right)=\frac{\phi V}{273+t_2},$$

or

$$=\frac{31068(273+t_2)}{V}\left(\frac{w_1}{d_1}+\frac{w_2}{d_2}\right)$$

$$= \text{total pressure—pressure of air in } V$$

$$=\frac{pL(273+t_2)}{l_c(273+t_1)}-\frac{p(273+t_2)}{273+t_1};$$

thus (substituting pL/L_c for p, and L_c for L) we have

$$d_2w_1+d_1w_2=\frac{d_1d_2pLV(L_c-l_c)}{31068\, l_cL_c(273+t_1)},$$

and $w_1 + w_2 = w$, whence w_1, w_2 can be solved.

Results

The heating liquid employed was water. The results are given as percentages, *i. e.*, as obtained by the further calculation of the quantities 100 w_1/w and 100 w_2/w.

Mixture	p mm	L mm	V cc	L_c mm	l_c mm	w grams	t_1 °C	Percentages
$(C_2H_5)_2O$ C_6H_6	755	320	98.5	322	178	0.2568	16.0	20.9 79.1
$C_2H_5.O.C_2H_5$ C_6H_6	755	318	95.1	321	169	0.2684	17.0	58.1 41.9
C_6H_6 $CH_3.OH$	759	294	90.3	298	141	0.1429	15.5	10.1 89.9
C_6H_6 $CH_3.OH$	759	280	88.4	285	130	0.2842	17.0	86.3 13.7

TABLE—(*Continued*)

Mixture	p mm	L mm	V cc	L_c mm	l_c mm	w grams	t_1 °C	Percentages
$CH_3.OH$ $C_2H_5.OH$	764	291	81.7	293	110	0.2164	16.5	50.0 50.0
$CH_3.OH$ $C_2H_5.OH$	764	300	77.6	303	111	0.1959	18.0	72.8 27.2
$C_2H_5.OH$ $CH_3.CO.CH_3$	761	289	72.9	291	108	0.2889	15.0	18.1 81.9
$C_2H_5.OH$ $(CH_3)_2CO$	761	311	68.2	315	119	0.2306	16.5	69.0 31.0
$CH_3.CO.CH_3$ CCl_4	758	281	93.8	284	153	0.3024	15.0	43.1 56.9
$CO(CH_3)_2$ CCl_4	758	282	90.0	286	145	0.2781	17.0	61.0 39.0
C_6H_6 $(CH_3)_2CO$	760	265	85.5	270	121	0.2804	16.5	37.8 62.2
CCl_4 C_6H_6	761	279	81.4	282	132	0.3138	17.5	8.3 91.7

Part IV[1]

The formula for calculating vapor-densities is independent of t_2, the temperature to which the bulb is heated; therefore, once the substance experimented on is completely vaporized, any variations in the temperature as a whole will produce no change in l (l being the only quantity which can thus be appreciably affected), assuming that the molecular constitution of the substance does not suffer alteration during such variations in temperature; hence there is no necessity

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[1] Compare Zeit. phys. Chem., 63, 635 (1908).

to use a heating medium boiling at constant temperature. This consideration points to a simple method for heating; the sealed bulb is placed in a wider piece of combustion tubing; a thermometer reading to 358° is put into another piece of tubing, to act as a safeguard against raising the temperature above 358°; the two are then placed horizontally side by side and heated by means of an ordinary combustion furnace, or better in a trough containing some substance (*e. g.*, glycerine) which can be heated to a high temperature.

No allowance is necessary for the vapor-tension of the mercury-thread, for the tension within the manometer is equalized by that in the bulb; further, the pressure within the bulb is so considerable (it may rise to as much as 5 atmospheres or even more—consequently the need for surrounding the bulb with the thick combustion tubing to guard against possible risk of bursting, although the author himself has not in a single instance met with such an accident, though he carried out over fifty determinations at fairly high temperatures, many of them well above 300°) that the bulb may be heated above 358°, the boiling point of the mercury under normal pressures.

Seeing that the bulb is heated in a horizontal position, no correction is required for *l*, the formula to be used in calculation being either

$$\frac{31068\,wlL_c(273 + t_1)}{pL(V + h)\left(L_c - l\,\frac{V + H}{V + h}\right)},$$

or preferably (because simpler and almost inappreciably less accurate)

$$\frac{31068\,wlL_c(273 + t_1)}{pLV(L_c - l)}.$$

There is no need, whatever, to graduate the capillary-tube, for it is a very simple matter to read L correctly by means of a mm scale, and L_c and *l* by the aid of a pair of calipers or compasses or dividers, the distance between the legs being then measured off along a mm rule or scale. (On account of the great heat, it is impossible to keep the eyes sufficiently near the bulb to observe the graduations if the manometer be graduated.) As the manometer consists simply of an almost inexpensive plain piece of capillary-tubing, it is most advisable to cut off the sealed end, thoroughly clean and dry the bore, and again seal one end every time before an experiment is performed.

From the results of experiments carried out (see the remarks further on) it is conclusively demonstrated that the method may, with safety, be used for determining the vapor-densities of substances which under ordinary conditions react chemically with mercury.

Not too long a thread of mercury should be introduced into the capillary, so that a good length of air-thread (*i. e.*, H) may be left between the open end of the manometer and the mercury-thread, for after sealing the bulb, L_c (Fig. 3) is invariably greater than L, and therefore, if no such provision (*viz.*, a fairly large value for H, from 2 to 3 cm) be made, some of the mercury from the thread may be expelled from the bore and fall into the bulb, thus spoiling the result of an experiment if the substance experimented on is capable of reacting upon mercury; otherwise (*i. e.*, when no such chemical reaction between the substance and mercury can take place) this overflow is of no importance, provided the mercury-thread is not entirely expelled from the bore.

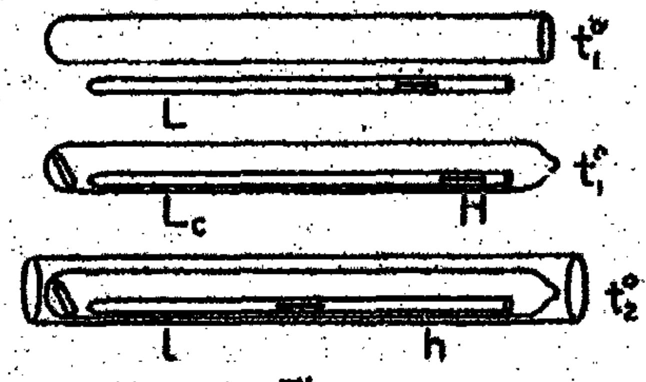

Fig. 3

It is, by far, more preferable to use a trough containing some liquid, that may be raised to and maintained at some convenient temperature than a combustion furnace as the heating medium; for, with the latter it is not a very easy matter to ensure that both the bulb and the manometer (which, in considering this question, it must not be forgotten, consists of a thick-walled capillary-tube) are at precisely the same temperature; of course, if the heating method as explained in Part II—(rather difficult of manipulation and calculation comparatively)—be used, this temperature difficulty entirely disappears, though, then the range of heating temperatures (t_2°), *i. e.*, the number of suitable heating liquids, as compared with a thermostatic method is rather limited. The thermostatic method is undoubtedly the best.

Results

The author employed in all cases a combustion furnace. The temperature was generally raised to about 50° above the temperature at which each respective substance vaporizes under ordinary atmospheric pressures; the flames were then turned out and the tubes covered with asbestos and left for about five minutes to allow both bulb and manometer to assume throughout as uniform a temperature as possible, after which l was measured in the manner indicated above. It will be observed that the substances experimented on are fairly representative, including organic and inorganic bodies, both solid and liquid substances.

Iodine gives such an extremely dark vapor that it was repeatedly found impossible to see the mercury-thread when the bulb was heated to the required temperature (t_2°). This difficulty was overcome by the following device. The manometer was pressed close to the bulb, prior to sealing, by resting it on two pieces of glass rod of suitable thickness; the bulb was then placed so that the manometer was to the top, and on heating it was found quite easy to observe both manometer and mercury-thread. All substances which give dark-colored vapors on heating, should be dealt with in this manner.

*Apparently no appreciable interaction took place between the mercury and these substances, probably owing to the small exposed surface presented by the outward end of the mercury-thread, and very likely also due to the prevention of diffusion of the vapors of these substances within the narrow bore of the capillary-tube and the interposition of

Substance	w gram	l mm	t_1 °C	p mm	V cc	L_t mm	L_c mm	Vapor-density	
								Found	Theory
C_5H_5N	0.0836	155	16.5	760	38.4	254	258	39.25	39.50
$C_5H_{11}.OH$	0.0763	165	15.5	763	30.0	268	277	44.16	44.00
$C_3H_5.OH$	0.0621	138	17.0	762	29.0	266	278	25.87	29.00
$(CH_3.CO)_2O$	0.1594	147	16.5	763	30.8	316	321	52.35	51.00
$CH_3.COCl$	0.1231	135	16.0	765	45.1	238	255	39.51	39.22
$CH_3.COH$	0.0340	128	15.0	756	36.6	190	192	22.22	22.00
H_2O	0.0346	161	16.0	753	44.3	326	329	9.01	9.00
$C_2H_4Cl_2$	0.1641	163	16.0	756	38.9	323	329	49.99	49.45
$C_2H_4Br_2$	0.0885	204	16.5	756	44.2	251	256	95.38	93.96
$CH_3.CO_2H$	0.0659	176	17.0	750	30.1	330	337	29.36	30.00
$C_6H_5.NH_2$	0.1208	193	16.5	761	29.5	380	390	48.66	46.52
$C_2O_2(O.CH_3)_2$	0.1722	177	16.5	761	40.0	326	340	58.83	59.00
$C_6H_5.NO_2$	0.1020	108	15.0	768	22.1	190	201	65.99	61.52
$CHBr_3$	0.1599	193	16.5	765	24.9	299	310	128.89	126.44
* $POCl_3$	0.1495	145	17.5	753	26.9	267	277	75.91	76.67
* PCl_3	0.1466	134	16.0	755	24.0	273	288	66.69	68.67
* § PCl_5	0.0727	163	17.5	760	22.6	271	285	51.63	104.12
* I	0.0879	160	23.5	760	22.1	205	230	123.6	126.8
* Br	0.1239	137	15.5	767	22.4	242	260	77.35	79.96
§ $CH_3.CH(OH).NH_2$	0.0355	167	18.0	760	38.6	283	294	14.94	30.52
$C_6H_4(OH).COH$	0.1390	174	19.5	760	34.1	325	334	54.47	61.00
$C_6H_5.COH$	0.1499	156	19.5	760	32.3	310	320	54.48	53.00
$CHCl_2.CO_2H$	0.1341	126	19.0	761	29.5	220	234	67.24	64.45
$CH_3.CO.NH_2$	0.1180	99	19.0	761	25.2	269	279	31.85	29.52
$C_6H_5.NH.CH_3$	0 1068	140	18.0	763	20.5	306	318	50.46	53.52
$C_6H_5.N(CH_3)_2$	0.1148	139	18.5	763	26.6	245	256	61.44	60.52
o-$CH_3.C_6H_4.NH_2$	0.1378	144	17.0	762	24.5	319	328	53.51	53.52
p-$CH_3.C_6H_4.NH_2$	0.1392	145	17.5	762	22.7	340	350	52.89	53.52
$(C_6H_5)_2NH$	0.1606	147	17.0	764	39.0	224	236	84.50	84.52
$C_6H_5.NH.CO.CH_3$	0.1700	129	18.0	766	36.1	232	241	66.50	67.52
§ $CCl_3.CH(OH)_2$	0.0895	143	16.5	765	29.4	229	240	55.29	82.67
$C_6H_5.COCl$	0.1542	165	16.0	763	26.8	326	335	67.53	70.22
$C_6H_5.CH_2Cl$	0.1479	141	17.0	763	24.5	296	306	62.97	63.22
p-$NH_2.C_6H_4.Cl$	0.1337	158	17.5	763	23.1	321	332	64.29	63.74
p-$CH_3.C_6H_4.NO_2$	0.1405	120	17.0	761	38.9	192	201	66.32	68.52
β-$C_{10}H_7.OH$	0.1296	117	18.0	765	34.2	180	194	73.34	72.00
α-$C_{10}H_7.NH_2$	0.1300	133	19.0	762	29.5	220	232	74.32	71.52

the long narrow cylindrical layer of air therein. Indeed, the fact that in these cases the vapor densities determined are not greater than the theoretical ones proves that no action between the mercury and these substances had taken place; for, had it been otherwise, it is quite evident that the loss of any of the substance in any particular case would have resulted in a lower pressure of vapor in the bulb with a consequent greater value for l, and therefore also a smaller value for $L_{c} - l$, than those theoretically required, both these quantities tending to make the calculated result greater than the theoretical one.

§ Evidently the PCl_5 dissociated into PCl_3 and Cl_2, and the $CH_3.CH(OH).NH_2$ into $CH_3.CHO$ and NH_3; in the case of the chloralhydrate about 57.6 percent of it decomposed into $CCl_3.CHO$ and $H.OH$ at the temperature of about 150°.

It will be found much more advantageous to use the method here given than that in Part III., as not only is it simpler and easier to calculate by its aid on account of its consisting of only one equation, but also it gives directly the percentage composition, whereas by the former method the percentage composition can only be obtained by further calculation.

Let w_1 be the percentage weight required of one of the constituents (of vapor-density d_1, supposed to be known), then $100 - w_1$ is that of the other component (of vapor-density d_2, also assumed known), and $w_1 + 100 - w_1$ or 100 is the total weight of the mixture. Now at 0° and 760 mm pressure

(1) the volume of the first component $= 11160\, w_1 \div d_1$;

(2) the volume of the second constituent $= 11160(100 - w_1) \div d_2$;

(3) the volume of the mixture $= 11160 \times 100 \div$ the vapor density of the mixture

$$= \frac{11160 \times 100 pLV(L_{c} - l)}{31068\, wlL_{c}(273 + t_1)};$$

but, (1) + (2) = (3); hence, on simplifying the resulting expression we obtain the equation

$$d_2 w_1 + d_1(100 - w_1) = \frac{100 d_1 d_2 pLV(L_{c} - l)}{31068\, wlL_{c}(273 + t_1)},$$

from which w_1, and $100 - w_1$, can be solved.

Mixture	p mm	L mm	V cc	L_c mm	l mm	w gram	t_1 °C	Percentages
$C_6H_5.CO.NH_2$	760	301	45.3	310	200	0.1504	18.0	45.84
$C_6H_5.N:N.C_6H_5$								54.16
m-$C_6H_4(OH)_2$	760	295	42.5	306	191	0.1487	18.0	27.85
$C_{10}H_7.Cl$								72.15
p-$CH_3.C_6H_4.OH$	765	293	40.9	301	187	0.1410	17.5	15.15
α-$C_{10}H_7.OH$								84.85
β-$C_{10}H_7.NH_2$	765	280	38.7	294	193	0.1572	18.0	34.60
p-$C_6H_4Br_2$								65.40
m-$HO.C_6H_4.CH_3$	763	295	36.1	308	188	0.1225	16.0	35.89
$C_6H_4(CO)_2O$								64.11
$C_{10}H_8$	763	210	33.8	220	128	0.1273	16.5	86.17
o-$NO_2.C_6H_4.OH$								13.83

The apparatus, and the equation above given, may be used in the study of the dissociation of decomposable compounds.

Part V[1]

The following apparatus will obviate the necessity for measuring V and for sealing the apparatus, though the introduction of the stopper will prevent its use at high temperatures (above 200°) due to risk of cracking the neck.

The bulb has at one end a conical mouth, the narrower end to face outwards with a perfectly ground, air-tight stopper to fit. When making the apparatus, the other end is sealed up after the stopper has been put in. The stopper should have a long handle of the shape shown to permit its being drawn outwards to close the mouth. After the manometer

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[1] Compare Zeit. phys. Chem., 63, 639 (1908).

and substance have been introduced the stopper is pulled into position; when heated the internal pressure of the contained air and vapor will fix the stopper tightly, the greater the internal pressure the closer the fit. To open the mouth again, the bulb is cooled, and the internal pressure diminished by cooling the bulb with a few drops of ether; on slightly tapping the stopper, it will be forced inwards by the relatively greater external pressure; it is advisable to wind loosely a piece of string round the handle of the stopper and the neck of the bulb, otherwise the stopper as it flies inwards may strike the bulb with sufficient force to break it.

Fig. 4

To test the air-tightness of the stopper, a little ether is poured into the bulb, the stopper fixed, and the whole immersed in warm water; if no bubbles of ether escape, the stopper fits properly.

The volume of the bulb is determined once for always. The stopper is fixed to prevent its moving, and the bulb placed in a vessel, mouth upwards; water is poured in to cover the stoppered bulb; the stopper is now allowed to fall down, and more water is added from a burette to fill the bulb and reach the same level as before; this extra volume of water represents the volume of the bulb. When working with it, allowance must of course be made for the volumes of the manometer and of the weighing-bottle.

The internal diameters of the neck and of the body of the bulb should be sufficiently large to allow the manometer to be inserted with ease and to get past the stopper without difficulty.

With this apparatus it will be found that L_t and L_c are equal (or generally very near so).

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A NEW METHOD FOR DETERMINING VAPOR-DENSITIES.[1]

BY PHILIP BLACKMAN

Part I

The method here described is one of the simplest, least expensive, and most accurate of all those hitherto discovered for determining vapor-densities. By means of it the actual volume of the vapor of a substance is directly measured.

Apparatus

A long tube A has one end, X, narrowed down leaving enough room for a Hofmann's weighing-bottle to pass through; the other end is drawn out to a long, thin, capillary-tube, Y, left open.

Method

The bottle containing the weighed substance is pushed through X, which is then connected by means of a piece of rubber pressure-tubing with another piece of long glass tubing B; both A and B are placed vertically, and mercury poured into B until the bottle in A rises to within about 8 cms from Y; the position of the level of the mercury in A is carefully noted with reference to some mark on the glass, and the capillary end Y is at once sealed off by placing a flame to it. The tube A is now surrounded with a suitable heating jacket, and heated in the vapor of some liquid boiling above the temperature at which the substance experimented on vaporizes (to aid evaporation, the pressure in A is reduced by removing some mercury from B or by lowering the latter tube). When the substance has completely vaporized, the

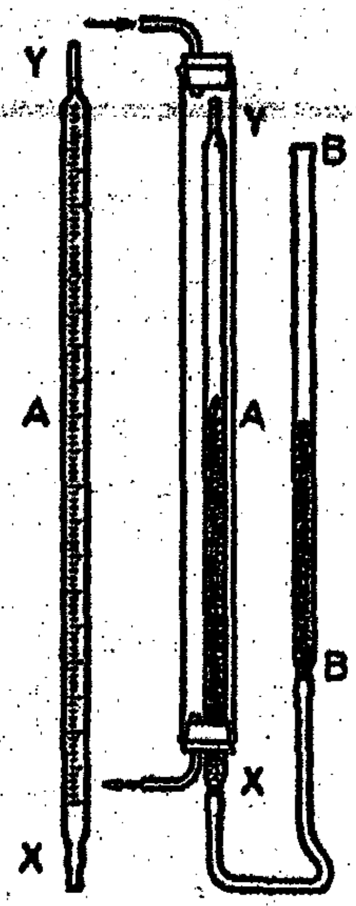

Fig. 1

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[1] Compare Ber. chem. Ges., Berlin, 41, 768 (1908).

mercury in B is brought on a level with that in A, the position of the level of the mercury in the latter being once more noted. (It is necessary to have some scale—any scale—etched on A to aid in observing the positions of the level of the mercury. A disused burette may with advantage be converted into the tube A, the tap being cut off and the glass fused to make an even smooth edge to serve for the end X, the other end being softened in the blowpipe-flame and drawn off).

The tube A is next disconnected and placed vertically with the open end X to the top. Mercury is poured in from a good burette (reading accurately to 0.05 or 0.025 cc) until the position on the tube is reached where the mercury stood first; the volume thus found is the volume of the air enclosed; more mercury is added until the second position is attained, and the volume of the total mercury represents the volume of the mixture of air and vapor.

Theory

Let $t_1°$ = the temperature of the air (when Y was sealed);
$t_2°$ = the temperature of the heating vapor;
v_1 = the volume of the air (at $t_1°$, as measured above);
v_2 = volume of the air and vapor (at $t_2°$, as found above);
w = weight of the substance;
p_1, p_2 = the initial and final atmospheric pressures, measured in mm (*i. e.*, when sealing the tube and at the end of the experiment, respectively; generally, $p_1 = p_2$.

The volume of the air at $t_2°$ =

$$\frac{p_1v_1(273 + t_2)}{p_2(273 + t_1)};$$

therefore, the volume of vapor at $t_2° = v_2$, volume of air at t_2 =

$$\frac{p_2v_2(273 + t_1) - p_1v_1(273 + t_2)}{p_2(273 + t_1)};$$

this volume, at 0° and 760 mm,

$$= \frac{273[p_2v_2(273 + t_1) - p_1v_1(273 + t_2)]}{760(273 + t_1)(273 + t_2)}.$$

Hence, the density of the vapor is given by this last formula divided into w; or, the vapor-density, compared with hydrogen at 0° and 760 mm (assuming 1 gram of hydrogen occupies 11160 cc) is given by the formula (to be used in practice)

$$\frac{31068\,w(273+t_1)(273+t_2)}{p_2v_2(273+t_1)-p_1v_1(273+t_2)}.$$

Precautions

(1) The amount of substance experimented on must be determined by the capacity of the apparatus.

(2) To use the apparatus for another experiment, it is only necessary to cut off the sealed end of the capillary-tube Y, and to thoroughly clean and dry the tube; when the capillary has become too short, the glass is softened in the blowpipe flame and drawn out to a fresh capillary.

(3) Any number of determinations can be made, without reweighings etc., by simply passing through the heating-jacket the vapors of various suitable heating liquids in turn.

(4) Dry, clean mercury only should be employed.

Results

If every precaution be taken to measure accurately the various quantities, no difficulty should be found in obtaining results which differ very slightly from the required theoretical values. A successful experiment should occupy about 45 minutes.

The author used water as the heating liquid (here $t_2 = 100°$).

Substance	v_1 cc	v_2 cc	p_1 mm	p_2 mm	t_1°	w	Vapor-density	
							Found	Theory
C_6H_6	4.8	40.15	762	762	16.0	0.0870	38.97	39.00
$(C_2H_5)_2O$	4.65	30.4	765	764	16.5	0.0567	35.24	37.00
$CH_3.CO.CH_3$	4.55	32.2	751	752	15.5	0.0495	28.92	29.00
$CH_3.OH$	4.4	39.7	759	759	17.0	0.0352	15.79	16.00
$C_2H_5.OH$	4.2	41.55	765	765	15.0	0.0529	22.21	23.00
$CH_3.CO.OC_2H_5$	4.05	29.8	767	766	16.5	0.0703	43.25	44.00
$CH_3.CN$	3.95	37.15	755	754	16.5	0.0409	19.62	20.52
CS_2	3.8	42.3	754	755	17.0	0.0901	37.01	38.06
C_2H_5I	3.6	35.0	749	750	14.5	0.1508	76.82	77.92
CH_3I	3.4	41.75	750	750	15.0	0.1727	71.44	70.93
C_2H_5Br	3.2	48.25	753	754	16.0	0.1591	55.41	54.48
$CHCl_3$	3.05	33.3	767	767	16.0	0.1085	55.84	59.67
CCl_4	2.95	27.05	767	768	16.5	0.1151	74.83	76.90

In conclusion, I beg to offer my thanks to R. Blair, Esq., Executive Officer of the London County Council, and to the Authorities of the Hackney Technical Institute, for the facilities granted to me to carry out the research.

Part II[1]

The following modified form of the apparatus, though somewhat more expensive and slightly less easy to manipulate, has nevertheless the advantage in that there will be no need to measure v_1 and v_2, neither will there be any necessity to seal the capillary Y.

The capillary-tube Y of A is replaced by a permanent thick-walled capillary-tube. To use the apparatus, the tube A must first be fixed in the heating-jacket, the capillary Y protruding through the other end; a small funnel is fastened to the capillary by means of a piece of rubber tubing; the rubber-tube can be closed by means of a clip or pinch-cock. The weighing-bottle and contained substance is introduced through the open end X, the pressure-tubing connecting with B fixed on, the clip at Y opened, and mercury poured in until the weighing-bottle reaches to nearly the capillary;

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[1] Compare Ber. chem. Ges., Berlin, 41, 770 (1908).

a little mercury is now poured into the funnel, and by lowering A a thread of mercury is drawn down to close the capillary, after which the clip is closed, and the heating process proceeded with.

The tube is permanently calibrated in cc (divided into smaller convenient divisions) from some definite mark on the capillary Y, the sealing-thread of mercury being always brought to this mark. Thus v_1 and v_2 can be directly read.

The heating-jacket and tube A may be made of jointed-glass (similar to a condenser), and in this case, as A would never have to be disconnected from the heating-jacket, the capillary-end Y may be terminated by a permanent funnel with a tap. With either of these two apparatus v_1 in any experiment may be made very small; indeed by the follow-device, v_1 can be made equal to zero (and the formula for the purpose of calculation reduces to $31068\,w\,(273 + t_2)/p_2v_2)$. The weighing-bottle is put in so that it will stand in A stopper downwards; also it must be quite full of the substance experimented on to exclude all air. The mercury is allowed to rise above the clip or tap, and the latter is then closed. Thus all air is removed from A. (If the weighing-bottle is placed stopper upwards, there is risk of the stopper coming out and the specifically lighter substance being forced out through the capillary.)

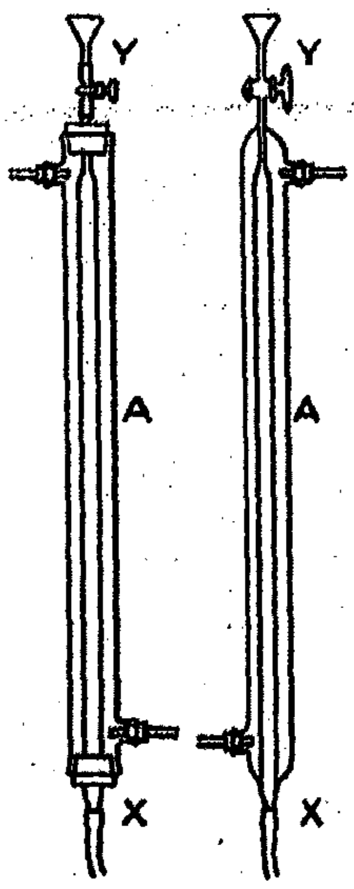

Fig. 2

In very accurate work, in v_1 allowance must be made for the volumes of the weighing-bottle and the substance contained, and in v_2 for the volume of the weighing-bottle. It may also be necessary to allow for the expansion of the glass of A and of the mercury in it.

Only pressure-tubing (with a very narrow bore) must be used to connect A and B; ordinary rubber-tubing (with a wide bore) is quite unsuitable, as it is difficult to fasten it quickly and securely to A and B, and also it is very liable to be distended by the weight of mercury thus introducing very appreciable errors.

Part III[1]

Apparatus

The apparatus consists of a thick-walled, long glass tube A, sealed at one end Y; the other end X is narrowed down, being left wide enough to allow a Hofmann's weighing-bottle to pass through; A is graduated in cms, beginning from Y. The end X can be connected by means of rubber pressure-tubing (100 cm in length) with a long glass tube B.

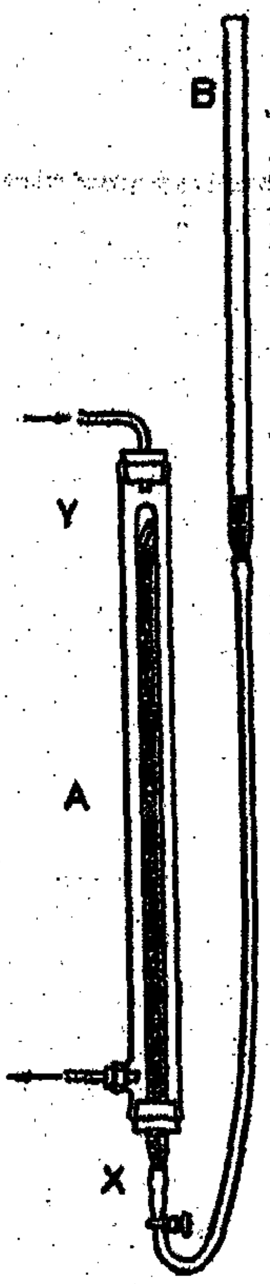

Fig. 3

Method

The pressure-tubing is fastened to B, which is fixed high up vertically; the other end of the pressure-tubing is closed by a clip or pinch-cock, and mercury poured into B until the pressure-tubing and part of B are filled. The tube A is placed upright, with X to the top, and filled nearly full with mercury; the weighing-bottle (containing the weighed quantity of the substance to be experimented on) is dropped in through X, the free end of the pressure-tubing pushed on to X, A inverted and fixed vertically with Y upwards (this will cause the weighing-bottle to rise to the top; if it sticks, it will move up if the tube A is tapped), the clip or pinch-cock opened, the mercury in A and B allowed to come to rest, the volume of air inclosed in A noted, and the difference in height between the mercury levels in A and B measured.

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[1] Compare Ber. chem. Ges., Berlin, 41, 881 (1908).

A is then surrounded by a suitable heating-jacket and heated in the vapor of some liquid boiling at a temperature above that at which the substance vaporizes. When the latter has completely vaporized, the volume of the mixture of air and vapor is observed and the difference in height between the mercury levels in A and B measured. B may be raised or lowered to various positions to obtain different readings for v_2 and m_2 (see below); v_1 and m_1 might similarly be varied, but this is inadvisable, as on diminishing the pressure, the substance may be caused to evaporate and thus v_1 would not represent the true volume of the enclosed air. It is best to hang a thermometer in the heating-jacket, whereby $t_2°$ may be correctly measured.

To clean the tube A, it is washed out with suitable solvents, ending up with a little pure ether; a long glass tube is introduced through X and a current of air forced through by means of a pair of bellows, to dry the interior of A.

Formula. (For the proof see Part II)

Let w = the weight of the substance;

p_1, p_2 = the respective initial and final atmospheric pressures;

m_1, m_2 = the differences in height between the mercury levels at the beginning and end of an experiment respectively;

v_1 = the volume of the air enclosed (at $t_1°$);
v_2 = the volume of the air and vapor (at $t_2°$);
$t_1°$ = the initial temperature of the air;
$t_2°$ = the temperature of the vapor;

the vapor-density is given by the formula

$$\frac{31068\, w(273 + t_1)(273 + t_2)}{(p_2 \pm m_2)v_2(273 + t_1) - (p_1 + m_1)v_1(273 + t_2)}$$

(+ m_2 when the mercury in B is on a higher level than that in A, and — m_2 when lower than that in A; when measuring m_1, the mercury in B should be on a higher level than that in A).

Results

The author used water as the heating-liquid (here $t_3 = 100°$).

	m_2	v_2	Calculated vapor-density
$CH_3.CO.CH_3$. $w = 0.0471$; $t_1 = 15°.5$; $p_1 = p_2 = 759$; $v_1 = 2.5$; $m_1 = 112$; theoretical vapor-density = 29.00	537	16.6	29.17
	404	18.5	29.15
	316	20.0	29.18
	101	25.0	29.19
	— 43	30.0	29.18
	—144	35.0	29.17
	—221	40.0	29.15
C_6H_6 (benzene). $w = 0.0511$; $v_1 = 3.0$; $m_1 = 40$; $p_1 = p_2 = 760$; $t_1 = 16°$; vapor-density (theoretical) = 39.00	472	15.0	38.50
	213	19.0	38.48
	164	20.0	38.49
	— 21	25.0	38.47
	—144	30.0	38.50
	—232	35.0	38.49
	—298	40.0	38.50
	—350	45.0	38.51
$(C_2H_5)_2O$. $w = 0.0522$; $v_1 = 3.5$; $m_1 = 29$; $p_1 = p_2 = 760$; $t_1° = 16°$; theoretical vapor-density = 37.00	573	15.0	36.82
	240	20.0	36.81
	40	25.0	36.81
	— 93	30.0	36.79
	—189	35.0	36.82
	—260	40.0	36.81
	—316	45.0	36.80
	—360	50.0	36.81

Part IV[1]

When tube A is being heated, it will be found that a few small bubbles of air, retained by the mercury, rise up and mingle with the air and vapor; their volume is very small, but it is advisable to allow for them by redetermining v_1 at the end of the experiment; to do so, tube A is allowed to cool down to t_1, the temperature of the air and tube B is raised till the

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[1] Compare Ber. chem. Ges., Berlin, 41, 1588 (1908).

mercury in it is on a level with that in A, when v_1 is read off afresh. (The increase in v_1 thus determined varies between 0.1 and 0.4 cc).

Seeing that the method permits of vaporizing substances under diminished pressure, *i. e.*, at $p_2 - m_2$, by using small quantities, substances may be completely vaporized at temperatures considerably below their ordinary (*i. e.*, at 760 mm pressure) boiling points. As illustrative instances, the following determinations were made at 100°.

Substance	w	$t_1°$	$p_1 + m_1$	$p_2 - m_2$	v_1	v_2	Vapor-density	
							Found	Theory
$CHBr_3$	0.0784	16	760	160	0.2	50	127.99	126.44
C_5H_5N (pyridine)	0.0349	14	754	250	0.3	45	38.56	39.50
$C_5H_{11}.OH$	0.0205	15	756	250	0.5	24	43.15	44.00

If every precaution be taken to measure accurately the various quantities, and also the following corrections be allowed for (a) the volumes of the weighing bottle and of the contained substance when measuring v_1, (*b*) the volume of the weighing bottle when measuring v_2, (*c*) the vapor tension of mercury above 100°, (*d*) the curvature of the mercury meniscus both for v_1 and v_2, (*e*) the expansion of the glass tube A and (*f*) the expansion of the mercury, the method may be used for determining accurately the constituents by weight of a mixture of two substances or to determine the amount of an impurity in a substance. Thus, let w_1, w_2, be the required weights of the two substances whose vapor-densities (supposed known) are d_1, d_2, respectively. Then v_2 (reduced to 0° and 760 mm) =

$$\frac{273v_2(p_2 \pm m_2)}{760(273 + t_2)};$$

v_1 (reduced to 0° and 760 mm) =

$$\frac{273v_1(p_1 + m_1)}{760(273 + t_1)};$$

the difference between these two quantities

$$= \frac{273}{760}\left\{\frac{(p_2 \pm m_2)v_2}{273 + t_2} - \frac{(p_1 + m_1)v_1}{273 + t_1}\right\}$$

= the volume of the vapor at 0° and 760 mm

$$= 1160\left(\frac{w_1}{d_1} + \frac{w_2}{d_2}\right);$$

by simplifying this equation, we obtain

$$d_2w_1 + d_1w_2 = \frac{d_1d_2[(p_2 \pm m_2)v_2(273 + t_1) - (p_1 + m_1)v_1(273 + t_2)]}{31068(273 + t_1)(273 + t_2)}$$

and $w_1 + w_2 = w$ (by actual weighing), whence w_1, w_2, can be solved.

In the following experiments, corrections (*a*) and (*b*) above mentioned were made. $t_2° = 100°$.

Substance 1 Substance 2	w	$t_1°$	$p_1 + m_1$ $=$ $p_2 \pm m_2$	v_1	v_2	w_1 w_2	Found w_1 w_2	Percentage error
$CH_3.CO.CH_3$	0.0656	15	774	3.25	33.5	0.0238	0.0246	+1.2
$C_2H_5.O.C_2H_5$						0.0418	0.0410	—1.2
C_6H_6	0.1286	13.5	764	3.3	35.9	0.0327	0.0326	—0.1
CCl_4						0.0959	0.0960	+0.1

Part V[1]

It will be found much more advantageous to use the method here given than that in Part IV, as not only is it simpler and easier to calculate by its means on account of its consisting of only one equation, but also it gives directly the percentage composition, whereas by the former method, the percentage composition can only be obtained by the

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[1] Compare Ber. chem. Ges., Berlin, 41, 1590, 2487 (1908).

further calculation of the quantities, $100w_1/w$ and $100 - 100w_1/w$.

Let w_1 be the percentage weight required of one of the components (of vapor-density d_1, supposed to be known), then $100 - w_1$ is that of the other constituent (of vapor-density d_2, also supposed known), and $w_1 + 100 - w_1$ or, 100 is the total weight of the mixture.

Now at 0° and 760 mm pressure

(1) the volume of the first constituent $= 11160w_1/d_1$;

(2) the volume of the second component $= 11160 (100 - w_1)/d_2$;

(3) the volume of the mixture =

$$\frac{11160 \times 100}{\text{vapor-density of the mixture}}$$

$$= \frac{11160 \times 100\{(p_2 \pm m_2)v_2(273 + t_1) - (p_1 + m_1)v_1(273 + t_2)\}}{31068\,w(273 + t_1)(273 + t_2)};$$

but, (1) + (2) = (3); hence, on simplifying the resulting expression, we get the equation $d_2w_1 + d_1(100 - w_1)$

$$= \frac{100d_1d_2\{(p_2 \pm m_2)v_2(273 + t_1) - (p_1 + m_1)v_1(273 + t_2)\}}{31068\,w(273 + t_1)(273 + t_2)},$$

whence, w_1 and $100 - w_1$, can be solved.

It should not be found difficult to so arrange the practical work that $m_1 = 0$, $m_2 = 0$ and $p_1 = p_2$ generally, that the calculations become much simplified. In the results here given, $t_2 = 100°$; also, the calculated percentage results are exactly identical with those as calculated by the equations in Part IV reduced to percentages.

Mixture	$p_1 = p_2$	m_1	m_2	v_1	v_2	t_1	w	Percentages
$CH_3.OH$ $C_2H_5.OH$	762	8	38	0.1	44.2	17	0.0628	26.14 73.86
C_6H_6 $(C_2H_5)_2O$	765	20	0	0.4	48.0	16	0.1250	41.22 58.78
$(CH_3)_2CO$ C_6H_6	760	0	—120	0.2	48.6	16	0.0882	52.01 47.99
CS_2 CCl_4	766	0	0	0.7	46.0	17.5	0.1264	82.33 17.67
$CH_3.COH$ $C_2H_4Cl_2$	767	0	0	0.3	49.5	18	0.0650	80.28 19.72

Part VI

The apparatus here described has this great advantage over those previously described: the difficulties of measuring air in the tube and making the necessary allowances in the calculations are absent. The method may also be looked upon as a modification or variation of Hofmann's apparatus.

A wide tube closed at one end A is filled with dry, clean mercury, and any air-bubbles are carefully removed. A small stoppered weighing-bottle completely filled (to exclude air) with the weighed quantity of substance to be experimented on is placed upon the mercury, and a rubber cork fitted with a glass U-tube (with narrow bore), flush with the stopper as shown (Fig. 4), is forced into the neck B of the tube, thereby pushing the weighing-bottle inwards and causing the excess of mercury to fill the U-tube and some to perhaps escape; the tubes should thus be air-free. The stopper should be tied on to the lip round the neck with wire and the tube inverted; if the weighing-bottle does not rise upwards, slight tapping on the tube-wall will cause it to do so. The tube is now surrounded with a suitable heating jacket and heated in the vapor of some liquid boiling at a temperature above that at which the substances vaporizes (Fig. 5). When the volume of the vapor in the tube remains constant, the position of the mercury-meniscus is noted and the difference in height (*m*) between the levels of the mercury in the U-tube and measuring-tube measured. The measuring-tube is removed, emptied of mercury, and (without removing the weighing bottle) water is poured in from a burette to reach the position the mercury occupied; the volume of the water gives the volume of the vapor.

Fig. 4

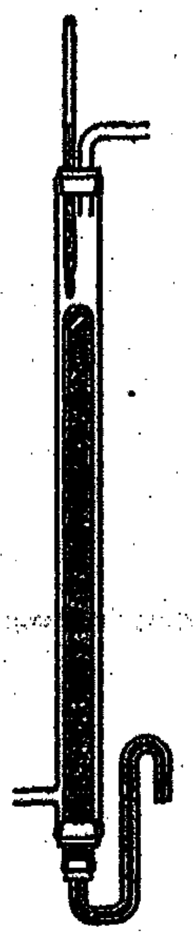
Fig. 5


Fig. 6

When the substance is vaporizing the overflowing mercury from the U-tube should be caught in a beaker.

If the U-tube be short and a wide tube attacked to it by means of a short piece of rubber pressure-tubing, mercury can be poured in so as to vary *m* (Fig. 6). This will be found especially useful if too great a quantity of substance has been introduced whose vapor would at comparatively low pressures occupy a larger volume than that afforded by the measuring-tube (compare first, second, ninth, and eleventh results).

If the measuring-tube be graduated in cc (from closed end) the volume of the vapor (subtracting the volume of the weighing-bottle) is read off directly.


Fig. 7

Fig. 7 shows how the measuring-tube may be made to consist of a thick-walled test-tube, and heated in a deep beaker. This simpler form must only be used with the following limitations: (1) the heating liquid must not act upon the rubber; (2) the temperature must not be raised too high to affect the rubber. The last two results were obtained with this apparatus.

Let w = the weight of the substance; v = the volume of the vapor; p = the atmospheric pressure; m = the difference in height between the mercury levels; t = the temperature of the heating-vapor; the vapor-density is given by the formula

$$\frac{31068\,w\,(273 + t)}{(p \pm m)v}$$

($+ m$ when the mercury-level in the measuring tube is on a lower level than that in the U-tube, and $- m$ when on a higher level).

The apparatus is very cheap, easily manipulated, and capable of giving quickly very accurate results.

For very accurate work the following corrections must be made: (*a*) for the vapor pressure of mercury above 100°; (*b*) for the curvative of the mercury meniscus; (*c*) for the expansion of mercury; and (*d*) for the expansion of glass.

Results

The average time of an experiment was about sixty minutes.

Substance	w gram	p mm	t °C	m mm	v cc	Vapor-density	
						Found	Theory
$CH_3.OH$	0.0842	761	100	+405	51.6	16.23	16.00
$C_2H_5.OH$	0.0869	761	100	+278	42.9	22.59	23.00
C_6H_6	0.0809	768	100	+ 32	30.0	39.06	39.00
CS_2	0.0865	760	100	+ 33	33.7	37.48	38.06
$C_2H_4Cl_2$	0.0821	759	100	− 13	26.3	48.49	49.45
$(C_2H_5)_2O$	0.0847	758	80	− 43	35.1	37.01	37.00
$(CH_3)_2CO$	0.0839	760	80	− 48	44.7	28.91	29.00
CH_3I	0.0877	760	80	− 94	20.3	71.14	70.93
$CH_3.CN$	0.0842	763	100	+360	40.2	21.62	20.52
CCl_4	0.0812	763	100	−163	20.1	78.02	76.90
$CHCl_3$	0.0878	764	100	− 47	24.1	58.88	59.67
$CH_3.CO_2C_2H_5$	0.0870	760	100	− 20	32.3	42.18	44.00
C_2H_5I	0.0812	764	100	+ 93	14.3	76.78	77.92
C_2H_5Br	0.0825	766	100	+111	19.6	55.62	54.48

100° = steam.
80° = benzene vapor.

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THE HYDRATES AND ACID SALTS OF FERROUS SULPHATE

FRANK B. KENRICK

A large number of ferrous sulphates have been described by various authors. The following are mentioned, with references, by Dammer:[1] $FeSO_4 7H_2O$, $FeSO_4 5H_2O$, $FeSO_4 4H_2O$, $FeSO_4 3H_2O$, $FeSO_4 2H_2O$, $FeSO_4 H_2O$, $FeSO_4$, $FeSO_4 H_2SO_4 6H_2O$, $FeSO_4 5H_2SO_4 5H_2O$ and FeS_2O_7. Many of these were prepared in contact with sulphuric acid of considerable concentration, and as this is extremely difficult to separate from the solid substance and as the analyses were often made after drying either by a current of air (Jeremin, $FeSO_4 H_2O$ and $FeSO_4 5H_2SO_4 5H_2O$)[2] or over concentrated sulphuric acid (Bolas, "Ferrous anhydro-sulphate," FeS_2O_7)[3], it is quite probable that the formulae given by these authors do not in all cases represent the true composition of the solid phases. The following experiments were carried out with the hope of fixing more definitely the composition of some of the ferrous sulphates stable in contact with solutions of sulphuric acid.

Method.—Powdered recrystallized ferrous sulphate ($FeSO_4 7H_2O$) was mixed with sulphuric acid of various concentrations in glass stoppered bottles and shaken at room temperature in a mechanical shaker until the composition of the liquid became constant. Glass marbles were added to each bottle to aid the stirring. To prevent oxidation, which in the longer experiments was found to be quite appreciable, the free spaces in the bottles were filled with nitrogen by blowing in a rapid stream of this gas before inserting the vaselined stoppers. The nitrogen was prepared from ammonium chloride, sodium nitrite and potassium bichro-

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[1] Handbuch anorg. Chemie, III, 329, 330, 337 (1893).

[2] Ber. chem. Ges. Berlin, 21, R, 590 (1888).

[3] Jour. Chem. Soc., 27, 212 (1874).

mate, washed by ferrous sulphate and soda lye, and kept in a gas-holder over weak lye.

After equilibrium was established and the bottles had stood upright for a day or so, the solid, which slowly settled to the bottom as a paste, was sucked up into a centrifuge tube. This was a cylindrical glass tube, temporarily closed at both ends by rubber stoppers carrying tubes of small bore. Immediately the tube was full, the temporary stoppers were replaced by rubber plugs faced with platinum discs. After centrifuging for 20 minutes, the plug at the upper end was removed, the liquid poured quickly into a weighing bottle and the plug immediately replaced. The other plug was next taken out, and the first plug pushed through the cylinder thus forcing out the cake of paste which was caught in the weighing bottle. In this way the contents of the centrifuge were transferred to the weighing bottles without more than a couple of seconds' exposure to the moisture of the atmosphere.

Determination of Composition of the Solid Phase.—Two methods were adopted for ascertaining the composition of the solid phases. Each alone is insufficiently accurate to settle definitely the composition, but together they afford a solution of the problem.

The first method consisted in analyzing liquid and wet solid over a range of varying composition of the liquid phase and obtaining the composition of the dry solid graphically from pairs of such analyses. Unfortunately, the difficulty of separating the liquid from the solid and the small range of concentration of liquid possible in some of the cases investigated combine to magnify enormously the effect of experimental error on the composition of the solid. For example, in the case of the compound $2FeO_3SO_32H_2O$,[1] taking the most favorable possible pair of analyses, an error of 0.1 percent in the determination of the SO_3 in one of the

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[1] With this substance, the paste always contained from 65–75 percent of liquid phase after centrifuging. Even after leaving it on a porous plate in an exsiccator over the mother-liquor as much as 60 percent remained.

pastes, would cause an error of about 6 percent in the ratio of H_2O to SO_3 in the dry solid. By the ordinary gravimetric method of determining SO_3 in the presence of iron it was not found possible to obtain results sufficiently accurate for the purpose, but a method based on specific gravity determinations, described below, proved quite satisfactory. (Duplicates agreed consistently to 0.1 percent.)

The second method adopted, consisted in adding to the mixture a "tell-tale" substance which dissolved in the liquid without entering into the composition of the solid phase, and determining the quantity of the liquid in the wet solid from the amount of the tell-tale found. For this purpose, ammonium sulphate was used. It was hoped that by using different tell-tales in duplicate experiments their non-participation in the solid could be proved from the identity of the composition calculated for the solid phase, but a satisfactory second tell-tale substance was not found. However, by adding the ammonium sulphate in small quantities after equilibrium was established the chance of its forming solid solutions was minimized. The far greater analytical errors of this method are partly compensated for by their much smaller effect on the result. For example, taking, as before, the case of $2FeO3SO_32H_2O$, an error of 0.1 percent in the SO_3 in the wet solid would cause an error of only about 1.5 percent in the ratio of H_2O to SO_3 in the dry solid. On the ratio of FeO to SO_3, both of which were determined directly, the effect of the error is much smaller, and the method serves to give this ratio with a fair degree of accuracy.

Composition by Specific Gravity Method.—Stock solutions of sulphuric acid and of ferrous sulphate were prepared and carefully analyzed—the former gravimetrically and the latter by permanganate. With these, a number of solutions were made up, all containing 0.000499 formula weights FeO per gram but varying quantities of SO_3. The specific gravity of these was found at 25.0° in a 20 cc pyknometer. The results are expressed by the interpolation formula:

$$y = 41.07 + 1.2643x - 0.001865x^2 + 0.000004257x^3,$$

where y = grams of SO_3 per kilo of solution and x = (sp. gr. × 1000) — 1080. The specific gravity is compared with water at 25° and uncorrected. In making the analyses of the wet solids, a weighed quantity of water, sufficient to effect solution, was added to the substance and the FeO determined in a portion of this liquid by $n/10$ permanganate. Enough water was then added to reduce the concentration of the iron to that to which the interpolation formula applied, and finally the specific gravity of the solution taken. The SO_3 in the wet solid was calculated from the formula, the FeO from the permanganate reading, and the water by difference.

The liquid phases, except those in equilibrium with tetra- and heptahydrates, contained only traces of iron. In these it was found that the SO_3 could be determined quite accurately with $n/5$ potassium hydroxide. The small quantity of iron was precipitated and oxidized to ferric hydroxide; directly, excess of alkali was added and had no effect on the end-point. The results of the analyses are given in the following table.

TABLE I[1]

Number	Receipt	Comp. of liquid. To 1 SO_3	Comp. of wet solid. To total of 1 formula weight	Solid phase
1	Residue[2] 370 cc acid[3] 120 cc fuming acid	1.122 H_2O 0.0002 FeO	0.0494 FeO 0.4835 SO_3 0.4671 H_2O	$FeO4SO_33H_2O$
2	Residue 450 cc acid	1.226 H_2O 0.0004 FeO	0.0428 FeO 0.4695 SO_3 0.4877 H_2O	$FeO4SO_33H_2O$

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[1] In Experiments 1–4 another interpolation formula was used corresponding to a smaller concentration of FeO. In Exps. 20–22 the SO_3 was determined directly as barium sulphate.

[2] By "residue" is meant the wet solid made by shaking 40 grams ferrous sulphate heptahydrate with 470 cc concentrated sulphuric acid and pouring off the liquid.

[3] By "acid" is meant chemically pure sulphuric acid, specific gravity 1.84.

TABLE I—(*Continued*)

Number	Receipt	Comp. of liquid. To 1 SO_3	Comp. of wet solid. To total of 1 formula weight	Solid phase
3	20 gram salt[1] 460 cc acid	1.275 H_2O 0.0005 FeO	0.0497 FeO 0.4632 SO_3 0.4871 H_2O	$FeO4SO_3 3H_2O$
4	Identical with No. 2 + 15 cc water	1.342 H_2O ? FeO	0.0434 FeO 0.4391 SO_3 0.5175 H_2O	$FeO2SO_3H_2O$
5	40 gram salt 400 cc acid	1.382 H_2O ? FeO	0.0737 FeO 0.4676 SO_3 0.4587 H_2O	$FeO4SO_3 3H_2O$ probably in unstable equilib.
6	20 gram salt 200 cc acid	1.407 H_2O 0.0008 FeO	0.1120 FeO 0.4550 SO_3 0.4330 H_2O	$FeO2SO_3H_2O$
7	30 gram salt 200 cc acid	1.456 H_2O 0.0009 FeO	0.1153 FeO 0.4482 SO_3 0.4365 H_2O	$FeO2SO_3H_2O$
8	45 gram salt 200 cc acid	1.595 H_2O 0.0013 FeO	0.1191 FeO 0.4372 SO_3 0.4437 H_2O	$FeO2SO_3H_2O$
9	55 gram salt 200 cc acid	1.637 H_2O 0.0014 FeO	0.0690 FeO 0.3902 SO_3 0.5408 H_2O	$2FeO3SO_3 2H_2O$
10	60 grams salt 200 cc acid	1.697 H_2O 0.0014 FeO	0.0634 FeO 0.3866 SO_3 0.5500 H_2O	$2FeO3SO_3 2H_2O$
11	85 grams salt 200 cc acid	1.822 H_2O 0.0011 FeO	0.0632 FeO 0.3678 SO_3 0.5690 H_2O	$2FeO3SO_3 2H_2O$
12	100 grams salt 200 cc acid	1.951 H_2O 0.0010 FeO	0.0636 FeO 0.3591 SO_3 0.5773 H_2O	$2FeO3SO_3 2H_2O$
14	90 grams salt 150 cc acid	2.209 H_2O 0.0011 FeO	0.0853 FeO 0.3442 SO_3 0.5705 H_2O	$2FeO3SO_3 2H_2O$

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[1] By "salt" is meant recrystallized ferrous sulphate heptahydrate.

TABLE I—(*Continued*)

Number	Receipt	Comp. of liquid. To 1 SO_3	Comp. of wet solid. To total of 1 formula weight	Solid phase
13	112.5 grams salt 150 cc acid	2.186 H_2O 0.0011 FeO	0.1770 FeO 0.3462 SO_3 0.4768 H_2O	Two phases: $2FeO3SO_32H_2O$ $FeOSO_3H_2O$
15	75 grams salt 150 cc acid 26 cc water	2.385 H_2O 0.0006 FeO	0.1496 FeO 0.3134 SO_3 0.5370 H_2O	$FeOSO_3H_2O$
16	75 grams salt 150 cc acid 41 cc water	2.685 H_2O 0.0004 FeO	0.1718 FeO 0.3016 SO_3 0.5266 H_2O	$FeOSO_3H_2O$
17	60 grams salt 120 cc acid 56 cc water	3.200 H_2O 0.0005 FeO	0.1366 FeO 0.2750 SO_3 0.5884 H_2O	$FeOSO_3H_2O$
18	60 grams salt 120 cc acid 80 cc water	3.921 H_2O 0.0006 FeO	0.1285 FeO 0.2531 SO_3 0.6184 H_2O	$FeOSO_3H_2O$
19	80 grams salt 100 cc acid 100 cc water	5.107 H_2O 0.0021 FeO	0.1119 FeO 0.2210 SO_3 0.6671 H_2O	$FeOSO_3H_2O$
20	28 grams salt 7 cc acid 15 cc water	7.93 H_2O 0.106 FeO	0.197 FeO 0.236 SO_3 0.567 H_2O blue crystals dried 1 FeO 1.001 SO_3 6.974 H_2O	Two phases: $FeOSO_3H_2O$ $FeOSO_37H_2O$
21	28 grams salt 7 cc acid 15 cc water	8.97 H_2O 0.142 FeO	Dried crystals 1 FeO 1.004 SO_3 4.15 H_2O	$FeOSO_34H_2O$
22	28 grams salt 3 cc acid 20 cc water	15.0 H_2O 0.287 FeO	Dried crystals 1 FeO 0.999 SO_3 7.11 H_2O	$FeOSO_37H_2O$

Explanation of Table I.—The numbers in the first column correspond with the numbers in the triangular diagram (See Figure) in which each corner represents one formula weight of the substance marked.

The second column contains the receipts by which the mixtures were made up (See foot-notes).

In the third column, the composition of the liquid phase is given in formula weights of H_2O and FeO to one SO_3.

Column four shows the composition of wet solid in formula weights of each constituent to a total of one formula weight (except in the case of the dried crystals, Exps. 20–22).

The last column shows the most probable formula of the solid phase.

Discussion of Results.—The lines for Exps. 1, 2, 3 and 5 meet very nearly in the point corresponding to the compound $FeO4SO_33H_2O$ (See Figure), and this formula is definitely confirmed by Exp. 23 of the next section (See Table II).

In Exps. 4, 6, 7 and 8, the lines converge in the direction of the point corresponding to $FeO2SO_3H_2O$, but the angle made by the lines is so small that the compounds $4FeO6SO_3H_2O$ or even the anhydrous $3FeO4SO_3$ (marked with crosses on the diagram) might also be said to represent the point of convergence. Exps. 24, 25 and 26 of the next section, fix the ratio of FeO to SO_3 as $FeO2SO_3$; hence the formula $FeO2SO_3H_2O$ represents the composition of the solid. The result of Exp. 4 is doubtful. The solid phase in the bottle was undoubtedly identical with that in Exps. 1, 2 and 3, both in texture of the paste and in microscopic appearance. The position of the points can only be accounted for by the assumption that the solid was in unstable equilibrium and changed in the centrifuge to the $FeO2SO_3H_2O$.

In Exps. 9, 10, 11, 12 and 14 the meeting point of the lines is not well-marked, probably owing to the large portion of liquid in the pastes analyzed, but the irregularity of the directions does not warrant the assumption of a solid solution. The points corresponding to the formulae $FeOSO_3$, $3FeO4SO_32H_2O$, $2FeO3SO_32H_2O$, $3FeO5SO_34H_2O$, $FeO2SO_32H_2O$, etc., in which the ratio of FeO to SO_3 increases from 1 : 1 to 1 : 2, all lie in the general direction of the lines. Exps. 27 to 30, below, point to the ratio $2FeO:3SO_3$ (possibly $3FeO:5SO_3$) as the most probable, corresponding with the formula $2FeO3SO_32H_2O$ (possibly $3FeO5SO_34H_2O$).

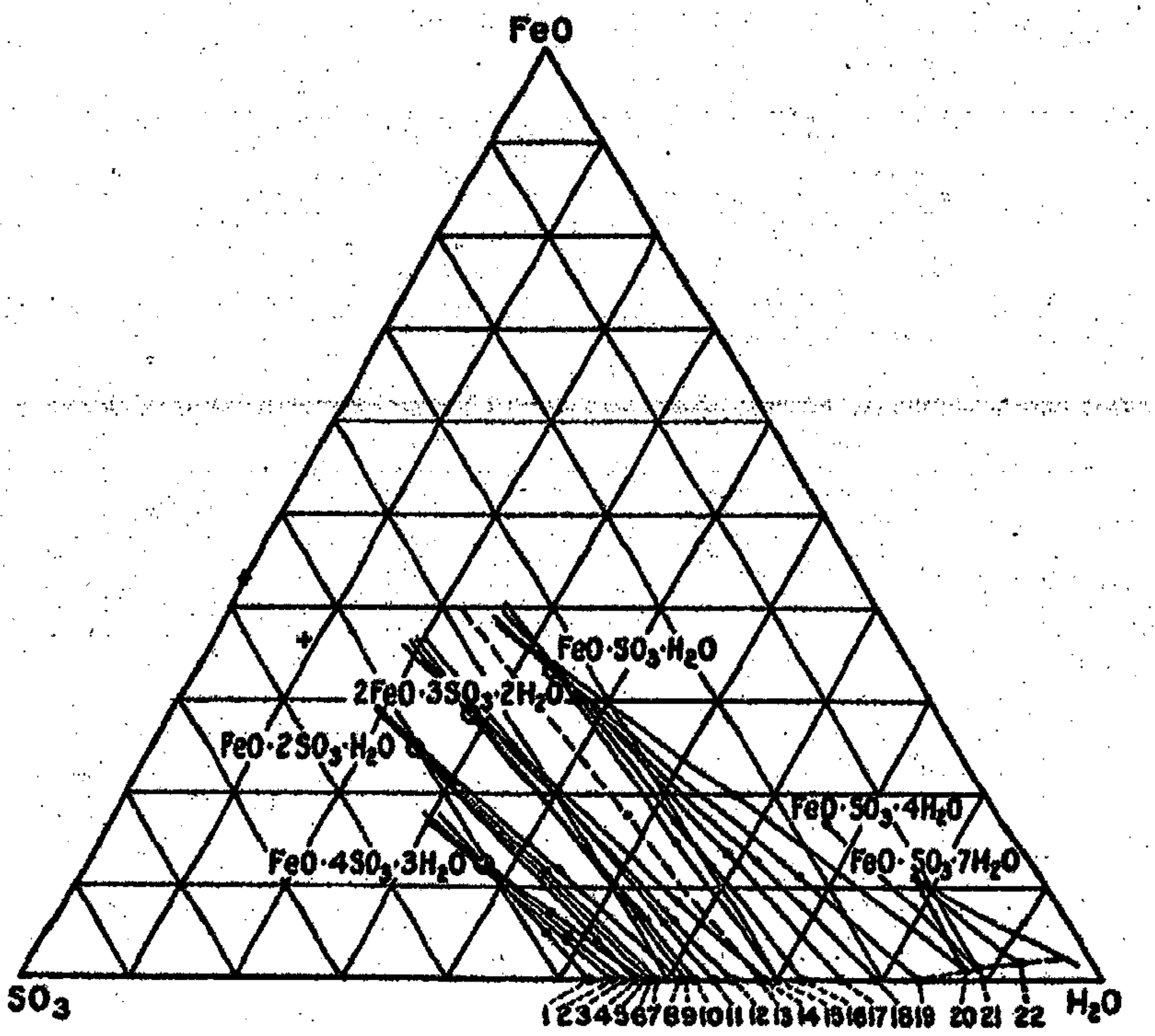

Fig. 1

In Exp. 13, two solid phases were distinctly seen under the microscope.

Exps. 15 to 20 leave little doubt that the corresponding solid phase in these cases is $FeOSO_3H_2O$. This formula is confirmed by Exp. 31, below.

In Exp. 20, the solid consisted of two phases, one, blue and the other white. The blue crystals were picked out, dried with filter paper, and found to be heptahydrate (in unstable equilibrium). The white paste was analyzed and gave the point in the diagram on the line drawn towards

$FeOSO_3H_2O$. On another occasion, the same mixture gave the result shown in Exp. 21, namely, the tetrahydrate. A detailed investigation of the salts in equilibrium with these weaker acids was not made.

Composition by Ammonium Sulphate Method.—In these experiments, FeO, SO_3, $(NH_4)_2O$ and H_2O were determined in both liquid and wet solid. The iron was determined by permanganate, the sulphuric acid as barium sulphate after removing the iron by precipitating twice with ammonia, and the small amount of ammonium by distilling with excess of lye and titrating the distillate. The water was determined by difference. The ratio of ammonium in liquid and wet solid, which unfortunately could not be determined very accurately, gave the amount of liquid in the wet solid. The results calculated for the dry solids are given in the following table. The values for the water, on which the effect of experimental error is greatest, are too inaccurate to be of much use, but the ratio of FeO to SO_3 is sufficiently accurate to enable one to decide between the various possible formulae given by the *direction* of the lines in the former method.

Explanation of Table.—The second column gives the receipts by which the mixtures were made up. For the meaning of the words Residue, Acid and Salt see foot-note to Table I. Under the heading "Ammonium Ratio" is given the ratio of $(NH_4)_2O$ in the wet solid to that in the solution, *per gram.*

The results have been discussed above in connection with the experiments in Table I.

Description of the solid phases.—The substance $FeOSO_3$ H_2O consists of very minute uniformly sized granular crystals about 0.001 mm in diameter. It is stable in contact with solutions of compositions from $SO_3 2.186H_2O$ to SO_3 $7.93H_2O$, at which point (in Exp. 20) the heptahydrate was formed. It is identical with the compound described by Jeremin[1] and may correspond with v. Bonsdorf's $FeSO_4H_2SO_4$ $6H_2O$, (A mixture of $FeOSO_3H_2O$ with 52.5 percent of solution $SO_3 6H_2O$ has this composition.)

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[1] Ber. chem. Ges. Berlin, 21, R, 590 (1888).

TABLE II

Number	Receipt	Comp. of liquid. Formula weights to 1 SO_3	Comp. of wet solid. Formula weights per gram	Ammonium ratio	Comp. of dry solid
23	Residue 400 cc acid 20 g Am. sulph.	1.23 H_2O 0.0004 FeO 0.0222 $(NH_4)_2O$	0.001051 FeO 0.00940 SO_3 0.00921 H_2O 0.000115 $(NH_4)_2O$	0.537	1 FeO 4.000 SO_3 2.7 H_2O
24	20 g Salt 200 cc Acid 20 g Am. sulph.	1.28 H_2O 0.0005 FeO 0.0414 $(NH_4)_2O$	0.001532 FeO 0.00892 SO_3 0.00903 H_2O 0.000244 $(NH_4)_2O$	0.621	1 FeO 1.99 SO_3 0.964 H_2O
25	20 g Salt 200 cc Acid 10 g Am. sulph.	1.304 H_2O 0.0005 FeO 0.0210 $(NH_4)_2O$	0.001665 FeO 0.00897 SO_3 0.00865 H_2O 0.000119 $(NH_4)_2O$	0.592	1 FeO 1.997 SO_3 0.77 H_2O
26	20 g Salt 200 cc Acid 10 g Am. sulph.	1.345 H_2O 0.0005 FeO 0.0213 $(NH_4)_2O$	0.002433 FeO 0.00849 SO_3 0.00783 H_2O 0.0000788 $(NH_4)_2O$	0.390	1 FeO 1.97 SO_3 1.18 H_2O
27	30 g Salt 50 cc Acid 3 g Am. sulph.	1.98 H_2O 0.001 FeO 0.0245 $(NH_4)_2O$	0.001036 FeO 0.00824 SO_3 0.0142 H_2O 0.000169 $(NH_4)_2O$	0.787	2 FeO 3.25 SO_3 0.6 H_2O

TABLE II—(*Continued*)

Number	Receipt	Comp. of liquid. Formula weights to 1 SO_3	Comp. of wet solid. Formula weights per gram	Ammonium ratio	Comp. of dry solid
28	35 g Salt 120 cc Acid 4 g Am. sulph.	1.66 H_2O 0.001 FeO 0.0145 $(NH_4)_2O$	0.001655 FeO 0.00826 SO_3 0.0116 H_2O 0.000083 $(NH_4)_2O$	0.633	2 FeO 3.04 SO_3 2.54 H_2O
29	55 g Salt 200 cc Acid 10 g Am. sulph.	1.62 H_2O 0.001 FeO 0.0220 $(NH_4)_2O$	0.00213 FeO 0.00820 SO_3 0.0102 H_2O 0.000098 $(NH_4)_2O$	0.695	2 FeO 2.94 SO_3 2.7 H_2O
30	30 g Salt 90 cc Acid 3 g Am. sulph.	1.69 H_2O 0.001 FeO 0.0144 $(NH_4)_2O$	0.001196 FeO 0.00846 SO_3 0.0128 H_2O 0.0000959 $(NH_4)_2O$	0.742	2 FeO 3.04 SO_3 2.63 H_2O
31	40 g Salt 50 cc Acid 50 cc Water 10 g Am. sulph.	4.74 H_2O 0.002 FeO 0.01121 $(NH_4)_2O$	0.00322 FeO 0.00589 SO_3 0.0156 H_2O 0.000298 $(NH_4)_2O$	0.466	1 FeO 0.987 SO_3 0.84 H_2O

The substance whose composition is probably $2FeO3SO_3 2H_2O$ consists apparently of fragments of small, extremely thin hexagons from 0.005 to 0.01 mm in diameter. Wet with the liquid phase, they form a very sticky paste. This paste was pure white in most cases, but in some of the earlier experiments where precautions were not taken to exclude the air; it had a distinct greenish tinge, possibly due to traces of ferric iron. It exists in contact with solutions $SO_3 1.637H_2O$ (about) to $SO_3 2.186H_2O$. It is probably the substance described by Jeremin[1] as "greenish shining crystals, very unstable," to which he assigns the formula $FeSO_4 5H_2SO_4 5H_2O$. This may well be so, since a mixture containing the compound with 71.3 percent of liquid phase (of composition $SO_3 2H_2O$) has the composition of Jeremin's substance, and it is "unstable" in the sense that a very slight absorption of water from the atmosphere would cause it to change to the granular $FeOSO_3H_2O$.

The compound $FeO2SO_3H_2O$ exists with solutions $SO_3 1.342H_2O$ to (about) $SO_3 1.595H_2O$. It consists of irregular groups of fine crystals of about 0.005 mm diameter, and is probably the "ferrous anhydrosulphate" of Bolas (FeS_2O_7) which he "dried" over concentrated sulphuric acid.

The compound $FeO4SO_3 3H_2O$ is stable with solutions ranging from the strongest one investigated, $SO_3 1.122H_2O$, to (about) $SO_3 1.342H_2O$. The crystals are fine needles, some of the largest being about 0.2 mm long. They dissolve rapidly in water, precipitating the $FeOSO_3H_2O$.

The solubility of all the compounds in the liquid phases (*i. e.*, the amount of FeO found in the liquids) is, except in the cases of the tetra and heptahydrates, very small. There is a maximum amount of iron at the point corresponding to Exp. 9, and a minimum point near Exp. 17.

Summary.—The compositions of a number of ferrous sulphates and their range of existence with sulphuric acid solutions at ordinary temperatures have been determined.

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[1] Loc. cit.

The composition of the solid phase was obtained by a combination of two methods of indirect analysis, each of which alone was insufficiently accurate for the purpose. In the first method, the analyses of liquids and corresponding wet solids gave the values of a and b in a number of equations to straight lines

$$y = ax + b,\ y = a'x + b',\ \text{etc.},$$

in which y = amount of FeO and x = amount of H_2O to $1SO_3$, and the points on which correspond to possible compositions of the solid phase. In some cases the values of x and y representing the composition of the actual solid, could be determined from the cutting point of these lines; in others the smallness of the angles made this impracticable. In the second method, each analysis of liquid and corresponding wet solid gave the value of y fairly accurately, although the value found for x was too inaccurate to be of any use. By combining the two methods and substituting the value of y given by the second method in any of the equations obtained by the first the value of x could be determined.

University of Toronto,
September, 1908.

THE BEHAVIOR OF COLLOIDAL SUSPENSIONS WITH IMMISCIBLE SOLVENTS

BY W. LASH MILLER AND R. H. MCPHERSON[1]

Now that the study of colloids is attracting general interest, and convenient methods have been devised for the preparation of colloidal solutions in solvents other than water, it seems desirable to study the behavior of such solutions when brought together, with a view to discovering, if they exist, cases of equilibrium analogous to the distribution of iodine between ether and water.[2]

The prevalent theory of colloidal solutions, which represents them as finely divided suspensions in an inert liquid, seems at first sight to negative the possibility of any such distribution. Graham's experiments,[3] however, and the more recent work of Linder and Picton[4] show that many colloids possess the power of diffusion, *i. e.*, that their chemical potential increases with increase of their concentration;[5] and as, from the point of view of the phase rule, a suspension whose potential depends on its concentration cannot be distinguished from the constituent of a "true" solution, the phenomena of distribution may as legitimately be expected in one case as in the other. Where the change of potential with the concentration is slight, *i. e.*, where the osmotic pressure is small (or the "molecular weight" of the solute or suspension is high), as in the case of the colloids, very slight differences in the properties—surface tension, dielectric constant (Perrin)—of the solvent might be sufficient to offset considerable changes

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[1] Read before the section for Physical Chemistry of the American Chemical Society, June, 1908.

[2] Mr. Manning finds that tannin is distributed between water and ether, ethyl acetate, amyl alcohol, etc.; the solutions have measurable osmotic pressure, however, and for other reasons tannin cannot be considered to be a typical colloid.

[3] Phil. Trans., 1861, 183; fully abstracted in Jahresber. 1861, 62–82.

[4] Jour. Chem. Soc., 61, 137 (1892).

[5] The theory advocated by Perrin, which endows the colloid particles with electrical charges, leads to the same conclusion.

in concentration; so that one would expect the distribution to be very one sided, and measurable only under special conditions. These considerations suggest that instances of the distribution of colloids between two solvents are most apt to be discovered by working with colloids of marked diffusibility, and with "immiscible solvents" of almost identical composition—such as the 'critical solutions' in two component systems (phenol, water) or the two phases at the plait point of the binodal curve in three component systems (water, chloroform, alcohol, etc.).

The experiments of Winkelblech on colloids and immiscible solvents made the probability of realizing the ideas set out in the preceding paragraph seem somewhat remote. In a paper published in 1906[1] that author describes "a hitherto unknown reaction for dissolved colloids" which consists in shaking the colloidal solution with petroleum, benzene, chloroform, carbon disulphide, or other immiscible solvent, whereupon the colloidal coagulates and collects in the emulsion which is formed at the surface of separation of the two solvents. This reaction leads to a delicate method for the quantitative determination of gelatine, and succeeds also with glutin, albumen, tannic acid, soluble starch, soap, wine, beer, water-glass, alkaline solutions of colophonium and of sulphur, and solutions of silicic acid in ammonia.

This reaction, if general, would make the experimental study of equilibrium in heterogeneous systems involving colloidal solutions difficult if not impossible. Winkelblech himself, however, has discussed an exception: shaking gelatine solutions with ether does not produce coagulation—and it seemed possible that among the colloidal suspensions (none of which were studied by Winkelblech) others might be found.

Silver, water, isobutyl or amyl alcohol

Our first experiments were tried with colloidal metals prepared by the methods of Bredig[2] and of Svedberg.[3] Silver

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[1] Zeit. angew. Chem., 19, 1953 (1908).

[2] Zeit. phys. Chem., 32, 127 (1902).

[3] Ber. chem. Ges., 38, 3616 (1905).

hydrosol is completely coagulated by shaking with commercial amyl alcohol or with isobutyl alcohol (traces of either of which much reduce the surface-tension of water); *shaking* however is necessary, merely pouring a layer of the alcohol over the hydrosol does not cause coagulation.

The 'isobutylalcosol' and 'amylalcosol' of silver by shaking with water, likewise are completely coagulated.

Silver, water, phenol

When phenol liquefied by a few drops of water is added to the hydrosol and a homogeneous solution formed by warming, no coagulation takes place even on standing; but if the solution is allowed to cool until it becomes milky from separation into two layers, and is then warmed again until homogeneous, all the silver is precipitated.

These experiments, while not resulting as had been hoped, show the dependence of the Winkelblech effect on the formation of surface, *i. e.*, on capillary forces, and serve to connect it with the separation of fibrin from blood by 'whipping' and with the formation of scum on the surface of streams near waterfalls and rapids.

Silver, water, chloroform, alcohol

When silver hydrosol is shaken with chloroform, very little coagulation takes place and none of the silver goes into the chloroform. Reciprocally, water does not attract silver from the 'chloroformsol.'

On adding alcohol to the systems: hydrosol-chloroform or chloroformsol-water, and shaking to secure equilibrium, most of the silver is coagulated, and what remains in suspension is retained by the layer of liquid in which it was originally present. The chloroform may be replaced by carbon tetrachloride and the silver by gold, without materially modifying the result. These observations seem important, but as it was not found possible to prepare metallic suspensions in chloroform or carbon tetrachloride free from tarry matter, too much stress must not be laid on them.

Arsenic trisulphide, water, chloroform, alcohol

This system is distinguished from the last by the much greater stability of the colloid; the hydrosol may be shaken with chloroform in presence or absence of alcohol, and homogeneous solutions may be "split" or rendered heterogeneous by addition of water or of chloroform without coagulation ensuing. It consequently seemed more suitable for the object in view, and the work with colloidal metals was discontinued.

In the preliminary experiments, whenever two liquid layers were formed the arsenious sulphide was always contained exclusively in the upper layer, no matter what the proportions of the reagents (aqueous solution of arsenious acid, hydrogen sulphide water, alcohol, chloroform). If distribution was to be observed at all, it was therefore necessary to find the proportions in which water chloroform and alcohol must be mixed to give two liquid layers of almost identical composition.

Determination of the binodal curve, tie-lines and plait-point

The system water-chloroform-alcohol has been studied by Bancroft[1] to whom in fact is due most of our experimental knowledge of similar equilibria; the data for the curve plotted in Fig. 1, however, were not taken from his measurements which were carried out in a thermostat at 20°, but were obtained directly by a series of determinations made without special precautions at room temperature. The abscissae give the volumes of chloroform (and hence of water, the sum in every case being 10 cc) and the ordinates the volumes of alcohol needed to produce homogeneity. The curve so obtained is the "binodal curve" of Schreinemakers.

When the volume of chloroform used was 3 cc or less, addition of alcohol caused the lower layer to gradually grow less and finally to disappear; when 4 cc or more was used, the upper layer disappeared. The abscissa of the "plait-

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[1] Phys. Review, 3, 120 (1895).

point" therefore must lie between 3 and 4. To find its position more accurately, 3.5 cc chloroform and 6.5 cc water were mixed in a tall cylinder of 25 cc capacity graduated in 1/10 cc, alcohol was added from a burette, and, after shaking, the volumes of the two phases were read (see Table 2). Then, through the point in Fig. 1 which represents the total composition of the system, a straight line was drawn terminated at either end by the binodal curve, its direction being so chosen that the lengths of the two portions (to right and left of the abscissa 3.5) stood in the proportion of the volumes of the upper and lower liquid layer respectively.

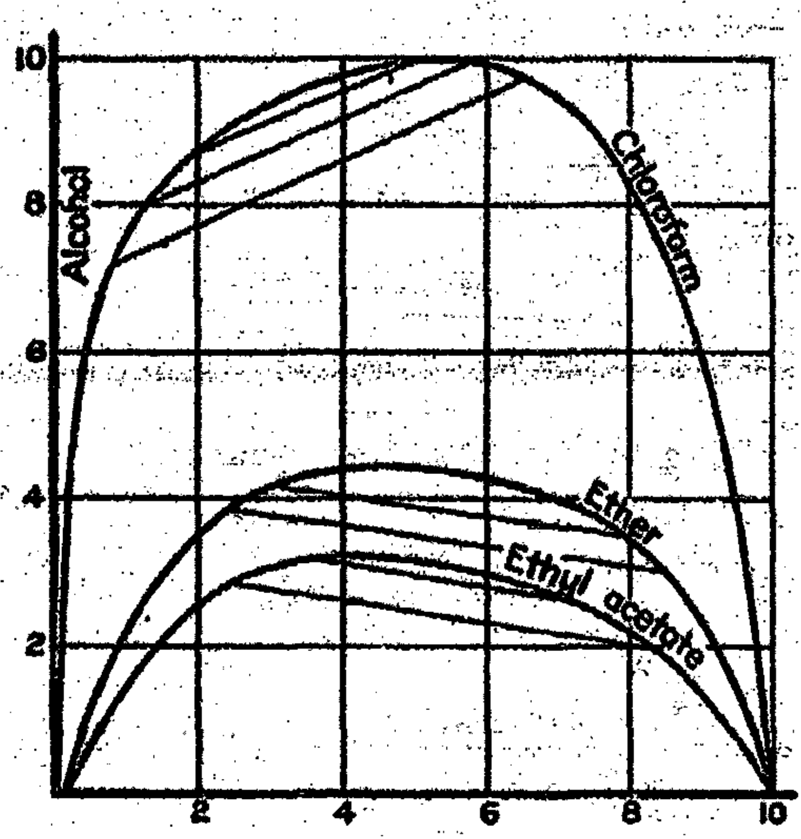

Fig. 1

If in place of the volumes of the two layers their weights had been determined—or what is the same thing, if their specific gravities were the same—the line so drawn would be a "tie-line" and its extremities would give the compositions of the two phases in equilibrium. Near the plait-point the compositions and consequently the densities of the two liquids are almost identical; lower down in the figure the graph gives only a first approximation to the compositions, which might be improved by introducing the densities calculated from the approximately known compositions of the two layers and the densities of alcohol water and chloroform, neglecting contraction on mixing.

The position of the "plait-point," *i. e.*, the composition of the system in which the two layers of liquid are almost identical in composition, was found graphically, and checked by direct experiment: it is chloroform 3.5 cc, water 6.5 cc, alcohol 9.8 cc.

Arsenic trisulphide, water, chloroform, alcohol, near the plait-point

Solutions were then made up containing 5.5 cc chloroform, 4.5 cc "water" (*i. e.*, 4.5 cc altogether of the solutions of arsenious acid and hydrogen sulphide in various proportions) and alcohol in quantity almost sufficient to make a homogeneous solution. The actual amount of alcohol needed depends on the temperature and also no doubt on the excess of arsenious acid or of hydrogen sulphide present, but it was not far from 9.6 cc. In no case was distribution observed; the sulphide always remained altogether in the upper layer, although in one experiment the compositions of the two phases were so nearly identical that partial separation was effected only by five minutes whirling in a good centrifuge (10 inch arm, 2000 rev. per minute) while complete separation needed a quarter of an hour. In this experiment the total volume was 15 cc, and the volumes of the two phases after separation were almost exactly equal; addition of less than 1/60 0.02 cc of alcohol made the whole homogeneous.

To ascertain whether the arsenious sulphide remained in the upper layer because of some "passive resistance," pairs of solutions—upper and lower—were made up from the data of Fig. 1, using pure water in the preparation of the "upper" and the solutions of arsenious acid and hydrogen sulphide in the preparation of the "lower" layers. On mixing, while the volumes of the two layers remained unaltered, the arsenious sulphide passed completely from the lower to the upper layers. "Passive resistances" therefore cannot be invoked to explain the very one sided distribution observed.

The slight difference in composition and properties of the two liquids evidently determined the distribution of the arsenious sulphide at equilibrium, from which it follows that the influence of the concentration of the latter on its chemical potential must be slight indeed—a calculation based on Perrin's theory and on measurements of the dielectric constants of the boundary solutions near the plait-point might lead to a lower limit for the 'molecular weight' of the sulphide.

Arsenic trisulphide, water, chloroform, acetone

The alcohol of the preceding sections was replaced by acetone; but, as before, the arsenious sulphide remained in the upper layer until the last drop of acetone removed the heterogeneity. The composition at the plait-point is: water 2.9 cc, chloroform 1.0 cc, acetone 8.1 cc.

Arsenic trisulphide, water, ether, alcohol

Tables 1 and 2 and Fig. 1 give the data for the binodal curve, tie-lines and plait-point. A glance at Fig. 1 shows that the ether curve is much flatter, *i. e.*, that in the system ether-water-alcohol, addition of a drop of alcohol produces more change in the compositions of the two layers than it does in the system chloroform-water-alcohol. To approach the plait-point by rough and ready methods is therefore much easier when chloroform is used than with ether; and from this point of view the latter system seem even less likely to afford instances of distribution than the former.

As a matter of fact, however, distribution was readily observed over a fairly wide range of composition on either side of the abscissa of the plait-point. The experiments were carried out by mixing measured volumes of 1 percent arsenious acid solution, ether, alcohol, and sulphuretted hydrogen water (either old or freshly prepared) in the order given, taking somewhat less alcohol than was necessary to make a homogeneous solution, and then adding more alcohol drop by drop, shaking, and letting stand until the two layers separated. As each drop of alcohol was added and the two layers approached one another in composition, the amount of arsenious sulphide in the upper layer increased until the colors of the two layers were almost equal. More of the sulphide went into the upper layers, other things being equal, when excess of hydrogen sulphide was used; but even with a considerable excess of arsenic (recognized by coagulating the sulphide with a drop of hydrochloric acid, filtering, and treating separate portions of the filtrate with arsenious acid and with hydrogen sulphide respectively) the distribution was easily observable.

Left to themselves, such two layered systems with distributed sulphide may remain for days apparently unchanged; but it was generally observed that sooner or later the upper layer lost its yellow color.

The upper layer is a very clear yellow with a touch of orange, and none of that milkiness usually observed with colloidal solutions; in this respect it resembles Linder and Picton's *Arsenious sulphide δ* which gave no Tyndall effect; the lower layer was almost equally clear. It is, in fact, only with such clear solutions that distribution was observed; if ether and alcohol were added to the ordinary boiled arsenious sulphide hydrosol, which relatively speaking is quite turbid, the sulphide remained in the lower layer until the last drop of alcohol made the whole homogeneous. By adding ether to a two-layered system, the volume of the lower layer may be diminished and the arsenious sulphide in it concentrated. When the concentration reaches a certain point, depending on the composition of the system, a trace of cloudiness may be detected, which increases with further addition of ether; the color at the same time changes from orange-yellow to a more lemon-yellow tint. It is thus possible to pass gradually, or 'continuously' so to speak, from perfectly clear to almost opaque colloidal solutions. Any one of these may be brought to the plait-point by adding alcohol and water in suitable quantities, distribution becoming less as the clarity of the solution diminishes.

The distribution of arsenic and sulphur between the two phases has not yet been studied; it is possible that even when arsenious acid and hydrogen sulphide have been added in equivalent quantities the upper layer may contain more sulphur than is equivalent to the arsenic it contains. Nor has the effect (if measurable) of the sulphide on the composition of the system at the plait-point, or on the temperature at which a system of given composition becomes homogeneous, been determined. These matters, together with a quantitative investigation of the effect of hydrogen sulphide on the distribution ratios will be taken up in this laboratory during the coming winter.

Arsenic trisulphide, water, ether, acetone

The composition at the plait-point is about: water 4 cc, ether 5 cc, acetone 8 cc. Distribution was observed.

Arsenic trisulphide, water, ethyl acetate, alcohol

See Tables 1 and 2 and Fig. 1. Distribution may be observed here also, though not so readily as when ether is employed. The observations are interfered with by the saponification of the acetate, which may render a heterogeneous system homogeneous on standing.

Arsenic trisulphide, water, ethyl acetate, propyl alcohol

The composition at the plait-point is about: water 12 cc, ethyl acetate 5 cc, propyl alcohol 7 cc. Distribution was observed.

Antimony trisulphide, water, ether, alcohol

A dilute solution of tartar emetic was substituted for the arsenious acid. Distribution was observed; after a few days the upper layer had become colorless, and finally all the antimony sulphide subsided from both layers.

Antimony trisulphide, water, chloroform, alcohol

No distribution was observed; the sulphide remains in the upper layer as is the case with arsenious sulphide. We intend to carry out similar experiments with benzene, carbon disulphide, etc., to see whether these substances resemble chloroform from this point of view.

Copper sulphide, water, ether, alcohol

A very dilute solution of copper acetate was used in place of the arsenious acid. No distribution was observed, the sulphide remaining in the lower layer although the plait-point was approached very closely. This agrees with Linder and Picton's opinion that colloidal solutions of copper sulphide are much further removed from the state of 'true' solution than are those of arsenious sulphide.

Summary

The occurrence of distribution of colloids between two immiscible solvents is not *a priori* impossible either from the point of view of the phase rule or from that of the electrified suspension theory of colloidal solutions. It may probably be easiest observed in the case of colloids with marked power of diffusion, and "immiscible solvents" which approach each other closely in properties and composition such as those near the 'critical solution temperature' in two component systems, or the solutions at the plait-point of the binodal curve in three component systems.

The Winkelblech effect interferes with the observation of such cases of equilibrium, for instance in the case of silver hydrosol and phenol, amyl alcohol, or isobutyl alcohol. Two experiments show the dependence of the Winkelblech effect on capillary forces.

Chloroform and alcohol do not coagulate the hydrosol of arsenious sulphide; but no distribution was observed even at the plait-point; this is not due to 'passive resistance.' The same is true when the alcohol is replaced by acetone; but if ether or ethyl acetate be substituted for the chloroform distribution readily occurs, whether the consolute liquid be alcohol, acetone, or propyl alcohol.

In this connection a rapid method of approximately determining the binodal curve, tie-lines, and plait-point is described.

Antimony trisulphide, like the sulphide of arsenic, distributes between the two liquid phases in the system water-ether-alcohol, but not in the system water-chloroform-alcohol.

Copper sulphide does not distribute in the system water-ether-alcohol.

TABLE 1

Binodal Curves, Room Temperature

Water cc	Chloroform cc	Alcohol cc	Ether cc	Alcohol cc	Ethyl acetate cc	Alcohol cc
9.5	0.5	6.3	—	—	—	—
9	1	7.7	—	—	1	1.2
8	2	8.7	2	3.5	2	2.7
7	3	9.4	3	4.2	3	3.1
6	4	9.8	4	4.4	4	3.05
5	5	9.9	5	4.4	5	3.1
4	6	10.0	6	4.2	6	2.9
3	7	9.4	7	4.0	7	2.7
2	8	8.2	8	3.5	8	2.2
1	9	6.0	9	2.4	9	1.4

TABLE 2

Tie-Lines

Water, 6.5 cc; Chl., 3.5 cc			Water, 5 cc; Ether, 5 cc			Water, 5.5 cc; Et. acet., 4.5 cc		
Alcohol cc	Lower cc	Upper cc	Alcohol cc	Lower cc	Upper cc	Alcohol cc	Lower cc	Upper cc
8.4	8.5	9.7	2.0	6.6	5.0	2.5	6.7	5.6
9.0	9.0	9.7	2.5	6.8	5.2	3.0	6.9	5.9
9.4	9.7	9.4	3.5	7.6	5.3	—	—	—
—	—	—	4.0	8.3	5.0	—	—	—

The University of Toronto,
June, 1908.

NEW BOOKS

A Text-Book of Organic Chemistry. *By A. F. Holleman. Translated from the Third Dutch Edition by A. Jamieson Walker, Assisted by Owen E. Mott. Second English Edition, Rewritten. 15 × 23 cm.; pp. xv + 589. New York: John Wiley & Sons, 1907. Price: $2.50.*—A good deal of physical chemistry has been incorporated into this book and apparently with great success. On p. 25 we find pressure-composition diagrams for systems of two miscible liquids having a maximum vapor pressure, having a minimum vapor pressure, and having neither maximum nor minimum. Perhaps in the next edition the author might point out that difference in boiling-points is not enough to make fractional distillation easy. An even more important point is difference in the composition of the co-existing liquid and vapor phases. One more line in each diagram and a few more lines of text would have brought this out clearly. Since the organic chemist invariably distils under constant pressure, it seems to the reviewer that the temperature-concentration diagrams would have been more helpful than the ones actually used.

On p. 27 we get an admirable statement of the theory of distillation with steam. On pp. 28–30 there is a good statement of the theory of 'shaking-out' though the reviewer thinks it could have been improved by the explicit statement that chloroform is preferable to ether when the substance to be shaken out is more soluble in it than in ether. So far as the reviewer's somewhat limited experience goes, each organic laboratory has a favorite solvent which it always uses regardless of whether it is the best in any given case or not.

On p. 35 we find the synthesis of methane by means of pulverulent nickel. On p. 85 we get Menschutkin's work on the rate of formation of tetra-alkyl ammonium iodides. On pp. 114–115 we have the dilution law in its application to organic acids together with the caution that it does not apply to strong acids. On p. 141 we have the equilibrium diagram for acetaldehyde and paraldehyde. This is but an earnest of what we may expect some day when organic chemistry shall really be studied in a systematic manner. On p. 159 under acetylene we find a reference to the limits of explosion for mixtures of air and acetylene, 3–82 % acetylene; also a reference to the danger resulting from the presence of calcium phosphide in calcium carbide. If the matter is to be gone into in such detail, a reference to the solubility of acetylene in acetone might well have been added.

On p. 199 there is a brief mention of the decomposition of oxalic acid and the oxalates by light. On p. 237 we have the migration of the ions as illustrated in the electrolysis of Fehling's solution. On p. 345 is given Tafel's work on electrolytic reduction of surine derivatives.

In an excellent chapter on the carbohydrates there are some paragraphs on the formation of optically active substances which are worth quoting in full.

"Investigation of the stereoisomerism of the monoses has contributed towards explaining the formation of optically active bodies in plants, while laboratory-syntheses usually produce the racemic forms; not, however, in artificial syntheses effected with compounds already having an asymmetric structure. Mannose, for example, yields mannoheptonic acid by the cyanhydrin-synthesis, and it would be expected, from analogy with other cyanhydrin-syntheses, that equal quantities of two stereoisomeric mannoheptonic acids would be formed. This is not so; only one acid is obtained, which shows that the building up of a molecule from one which is asymmetric can continue in an asymmetric sense. If an optically active compound were converted into a derivative with a greater number of asymmetric carbon atoms than itself, and if it were possible so to decompose the molecule of this derivative as to regenerate the original active substance, the residual part of the molecule would also be optically active. *One optically active molecule would thus have occasioned the formation of another.*

"The formation of sugar in the plant has been proved by vegetable physiologists to take place in the chlorophyll-grains, which are composed of optically active substances. It may be assumed that the production of sugar results from a combination of carbon dioxide or formaldehyde with these substances, their asymmetry making the sugar formed by the condensation also asymmetric. As the other constituents of plants are probably formed from sugar, their optical activity is easily understood, since they are formed from optically active material.

"How the first optically active compound arose, and how nature has not produced the chemical-mirror images of all optically active substances found in the existing flora and fauna, since, as far as is at present known, the probability for the formation of both must have been equal, are problems by no means solved by the foregoing considerations."

This quotation may serve also to illustrate the English style though it is only fair to say that the last paragraph shows the translator at his worst.

Wilder D. Bancroft.

Organic Chemistry, *Including Certain Portions of Physical Chemistry for Medical, Pharmaceutical, and Biological Students. By H. D. Haskins and J. J. R. MacLeod. 13 × 19 cm.; pp. xi + 367. New York: John Wiley and Sons, 1907. Price: $2.00 net.*—This is a much less important book than that of Holleman and it is unfortunately a much less satisfactory one. After reading the book, one begins to wonder why the student should not learn some physical chemistry before he takes up organic chemistry. The chapter on molecular weight determinations, the theory of solutions, and the properties of colloids is not a structural part of the book and is not even accurate. On p. 45 the authors say that "the amount of this lowering, or *depression of the freezing-point,* is proportional, not, in general, to the chemical nature of the substance, but to the number of molecules of substance dissolved in a given volume." The same error occurs on the next page in a more explicit form. "An interesting explanation of the fact that *C* is quite different for different solvents is furnished in Raoult's extension of his law: if a gram-molecule of a compound be dissolved in 100 gram-molecules of solvent (except water), the freezing-point of the latter will be depressed by about 0.02°." On p. 54 is the unsupported statement "that the essential feature of colloidal solutions is the large size of the molecules or aggregates of molecules. These are especially large in hydrogels, but they may be broken up into smaller aggregates by warming; hence a hydrosolgel becomes a hydrosol by the aid of heat."

The following quotations will illustrate certain peculiarities in the point of view. On p. 58 the authors say: "We see then that the structural formula is not only a graphical expression of the actual number of the various atoms in a molecule of the substance, but it is also an epitome of the more important reactions of the substance." This is putting the cart before the horse in great style.

The unfortunate student is likely to have trouble with the first paragraph on p. 60. "Before attempting to study the various organic substances individually, it is essential that we possess a general idea of their relationship to one another. Their number is so great that, did we attempt to remember the properties and reactions of each organic substance separately, we should utterly fail, and should, moreover probably overlook one of their most important characteristics in contrast with inorganic substances, *viz.*, their transmutability into other organic compounds. In inorganic chemistry it is impossible to convert the compounds of one element into those of another element, except by substituting the elements. Each element has its own fixed chemical properties and compounds. In organic chemistry, on the other hand, as remembered above, we may consider all our substances as compounds of the element carbon and as being, therefore, convertible into one another." *Wilder D. Bancroft.*

Feste Lösungen und Isomorphismus. *By Giuseppe Bruni. 14 × 22 cm; pp vi + 130. Leipzig: Akademische Verlagsgesellschaft, m. b. H., 1908. Price: paper, 4 marks; bound, 5 marks.*—In the autumn of 1907 Professor Bruni delivered a lecture on solid solutions before the Chemical Society of Breslau. This volume is based on that lecture, though much amplified and provided with a wealth of explanatory foot-notes. The first thirty pages deal with the general characteristics of solid solutions. Then come seventeen pages on crystalline form and chemical constitution, which are followed by thirty pages on crystalline form and the formation of solid solutions. As the reviewer has so often remarked, monographs of this type are much needed and we cannot have too many of them provided they are well written. This particular one is a satisfactory one. The author has played an important part in the development of the subject; he has been on the right side in the disputed questions; and he presents his subject in a clear and orderly manner.

In one point the author goes a little further than our knowledge quite justifies. When speaking of solid solutions having a maximum melting-point, p. 31, the author inclines to the belief that we are dealing with actual compounds and he remarks that "we are thus led to assume a kind of intermediate thing between a compound and a solution." It would have been much better to have pointed out frankly that we cannot at present distinguish between the hypothetical cases of two components forming a continuous series of solid solutions and of two components each forming a continuous series of solid solutions with a compound. This would have been the more desirable because people are continually telling us what are the constituents of a series of solid solutions even though there is often no evidence whatsoever in favor of their statements. Copper and zinc form six series of solid solutions; but there is no way at present of telling whether these different series of solid solutions are due to imaginary allotropic forms of copper and zinc, to unknown hypothetical compounds, or to some other cause. In the copper tin alloys we have a definite compound Cu_3Sn which differs in all its known properties from the particular solid solution which has the same analytical composition.

The author points out, p. 43, that isomorphism originally referred only to cases in which two substances have similar constitution and similar crystalline form. Many chemists now use the term as connoting the power to form solid solutions. Since these two requirements do not necessarily hold simultaneously, the author proposes the term "isogonism" instead of isomorphism as used by Mitscherlich and "synmorphism" to denote that two substances crystallize together. The word isomorphism would seem to drop out entirely under this arrangement. That would be distinctly undesirable and probably is not what the author intends. It was desirable, however, to lay stress on the loose way in which the word "isomorphism" is now used. It is much to be hoped that chemists and mineralogists can get together and decide on a fairly strict definition of the word.

Wilder D. Bancroft.

Quantitative Analyse durch Elektrolyse. *By Alexander Classen. (Fünfte Auflage in durchaus neuer Bearbeitung). 14 × 21 cm; pp. xii + 336. Berlin: Julius Springer, 1908.*—About one-third of the book is taken up with an introduction which seems superfluous because most people who will use the book do not need it while those who do need it can find it more accurately elsewhere. On p. 10 it is stated that a current which would precipitate 107.93 g. of silver from a silver nitrate solution would precipitate 18.63 g. of iron from ferric chloride solution. The fact is quite overlooked that iron does not precipitate from a ferric chloride solution. On p. 31, the author overlooks the formation of cuprous chloride in the electrolysis of cupric chloride solutions. On p. 65, the author says that there is still much in regard to the theory of rapid precipitation which needs explanation; but there is nothing to show what these alleged difficulties are. On p. 55 it is misleading to say that too rapid a precipitation of metal leads to a bad deposit. If the composition of the solution at the cathode is kept constant, the experimental evidence is all to the effect that there is no appreciable electrolytic time-factor. On p. 87 it is difficult to make anything out of the statements in regard to the evolution of hydrogen and nowhere in the book has the reviewer been able to find any statement as to the importance of hydrogen evolution in connection with the electrolytic separation of two metals. These errors and omissions are merely the result of carelessness or ignorance. A more serious matter is the clever and consistent way in which the author treats the work done elsewhere, and especially that done at the University of Pennsylvania. It is true that the other work is cited; but it is cited in such a way to give an absolutely inaccurate impression of the real development. Page 111 may be taken as an instance of what is meant, though page 65 is not much better since no reference is made to page VI of the preface.

The working part of the book is satisfactory, though it suffers by comparison with E. F. Smith's book. Besides the sections on determinations and separations, there is also a section dealing with the analysis of such things as commercial copper, copper matte, bronzes, bearing metals, iron ore and steel, chrome nickel steel, manganese silicide, etc.

Wilder D. Bancroft.

Elektrochemie, II. *Experimentelle Elektrochemie, Messmethoden, Leitfähigkeit, Lösungen. (Sammlung Göschen, No. 253). By Heinrich Danneel. 10 × 15 cm; pp. 158. Leipzig: G. J. Göschen' sche Verlagshandlung, 1908. Price: bound, 80 pfennigs.*—This second volume contains chapters on electrochemical measurements, the conductivity of electrolytes, and the electrochemistry of solutions. When one considers the small size of the pages, one is forced to admit that the book is a marvel of compactness. The author's remarks on the conductivity of non-aqueous solutions, p. 87, and on the dissociating power of solvents, p. 93, are worth reading as unusually fair statements of the facts.

Wilder D. Bancroft.

Josiah Willard Gibbs *a propos de la Publication de ses Mémoires Scientifiques. By P. Duhem. 16 × 25 cm; pp. 43. Paris: A. Hermann, 1908. Price: paper, 2 francs.*—In this brief sketch Duhem lays especial stress on the two points that Gibbs was essentially an algebraist and that "his mind was of a retiring disposition." The following paragraphs give an excellent idea of certain aspects of Gibbs's work.

"Gibbs liked to contemplate truth, not in the variable and changing multiplicity of particular propositions but in the fixed and immovable unity of the general proposition. His thought did not try to reach out, even into wider developments of its consequences, but concentrated itself on the effort after a more abstract statement of the principles. This tendency characterizes the customary course of his genius. We have just recognized it in the method which he followed in announcing the results of his theories; we shall find it again, not less clearly marked, in the form to which he has given to the hypotheses from which these theories were devised." . . . .

"When the New Haven professor develops a physical theory, the hypotheses on which he bases his theory are always brought to the highest degree of generality while being reduced in number to a minimum. Sometimes a slightly greater restriction on these hypotheses would enable the imagination to help out the mind in its effort to grasp them; sometimes the citation of a particular case would serve as an illustration of the general case and would help one to understand the latter. Gibbs never consents to impose such restrictions and he never condescends to give such examples."

While discussing the development of the phase rule by van der Waals and Roozeboom, Duhem writes:

"M. Le Chatelier said with truth that Gibbs, by enunciating the phase rule, had done chemistry a service comparable to that which Lavoisier had rendered by formulating the law of the conservation of mass; but our legitimate admiration for the mathematician of New Haven, who wrapped the precious kernel in the hard rind of his algebraical formulas, should not interfere with our gratitude to the two Dutch chemists who crushed the ore and brought the pure metal to the sight of all.

"M. van der Waals showed a remarkable perspicacity in discovering the phase rule among the algebraical formulas where Gibbs had, so to speak, hidden it. This same perspicacity came to the aid of the learned Dutch physicist on another occasion. When he undertook to study the laws which govern the liquefaction of a mixture of two gases, it was from the famous memoir of the

Yale professor that he took the conception of the critical state of such a mixture. Since that time the physicists of Leiden and of Amsterdam have been busied with the study of the surface corresponding to one of the functions defined in that memoir, the function Ψ.

"But though M. van der Waals was clear-sighted enough to discover some of the ideas which were present as germs in the equations of Gibbs, and though he had the skill to make them produce the experimental discoveries which were latent in them, how many similar seeds have remained sterile because no physicist and no chemist perceived them under the algebraical covering which hid them: The fruitfulness with which they were endowed has been recognized too late when the discoveries which should have resulted from them had already been made without reference to them." *Wilder D. Bancroft.*

Guide de Préparations Organiques *a l'Usage des Étudiants. By Emil Fischer. Traduction autorisée d'après la septième édition allemande, par H. Decker et G. Dunant. 12 × 19 cm; pp. xvii + 110. Paris: Gauthier-Villars, 1907. Price: paper, 2.50 francs.*—Since the German edition of this book is well known in this country, the special interest about the French edition lies in the following remarks made by the translators in the preface:

"Of late years there has been a movement against the use of laboratory manuals. It often happened that students made all the preparations in a mechanical manner without concerning themselves with the literature and without taking the trouble to observe the phenomena which occurred during the course of the experiment. We find that manuals which give theoretical details, have the fault of not making the student find for himself the explanation of the preparations he has made, either in the works on organic chemistry or in the original literature. Other manuals go to the other extreme, giving only easy preparations, involving neither theoretical interest nor a methodical gradation in the experimental difficulties. In view of the great development in laboratory teaching, the use of a manual has become necessary. It represents a great economy of time and of labor for the assistant and permits him, by this fact alone, to direct his efforts towards the development of a certain manual dexterity and of the power of observation so essential to a chemist."

Wilder D. Bancroft.

Handbuch der anorganischen Chemie. *Herausgegeben von R. Abegg und Fr. Auerbach. In vier Bänden, zweiter Band, erste Abteilung: Die Elemente der ersten Gruppe des periodischen Systems; 18×25 cm; pp. xiii + 867. Leipzig: S. Hirzel, 1908. Price: paper, 24 marks; linen, 26 marks.*—In this portly volume we have the subheads: hydrogen (Baur); lithium (Auerbach and Brislee); sodium (Hinrichsen); potassium (Hinrichsen); colloidal chemistry of the alkali metals (Lottermoser); rubidium (Hinrichsen); caesium (Hinrichsen); copper (Donnan); colloidal chemistry of copper (Lottermoser and Donnan); silver (Baur); colloidal chemistry of silver (Lottermoser); gold (Wohlwill); colloidal chemistry of gold (Lottermoser); while Brauner has charge of the sections on atomic weight determinations. The volume is an excellent one, the sections on copper and on the colloidal metals being exceptionally good.

Throughout the book Brauner takes the stand that the atomic weight determinations of Stas are inaccurate and that the values obtained by Richards and his pupils are the closest approximations to the real values which we have. This seems a reasonable attitude. We know of certain errors in Stas's determinations. Of course he may have made other errors which we do not know about and which may have just counterbalanced the errors we know about; but this is very improbable indeed. On the other hand, there may be errors in the work of Richards which we do not yet recognize. This is quite conceivable and should make us cautious in talking about probable error. However this may be, there is no question but that the work of Richards is by far the most accurate that we have. In order to keep in touch with the international atomic weight commission, Brauner gives two sets of atomic weights, one based on Ag = 107.930, the other on Ag = 107,883. The first set he calls the 'ancient' values and the second the 'modern' values.

Among the good features of the book are the discussions: of excess voltage, p. 86; of the equilibrium between copper, cupric salt and cuprous salt, p. 477; of the corrosion of copper, p. 559; of the oxidizing and catalytic action of copper salts, p. 569; and of the copper-iron equilibrium, p. 572. Anybody who is interested in such things will do well to compare the section on cuprous hydroxide, p. 583, with the corresponding one in Dammer's Handbuch. The chapters on the chloride, bromide, and iodide of silver are as satisfactory as one can expect in view of our shocking ignorance in regard to these salts.

In the article on sodium, the reviewer found a few statements with which he could not sympathize. On p. 209 the author says that sodium is made commercially, chiefly by the electrolytic processes of Castner, Grabau, and Borchers. Two paragraphs are then given to the commercial production of sodium by electrolysis of fused sodium chloride. No one could possibly guess from this that Castner's process is the only commercial one and that no sodium is made commercially by the electrolysis of fused sodium chloride.

On p. 217 is the statement that we cannot determine the dissociation of strong electrolytes from conductivity measurements because the values thus obtained do not accord with Ostwald's dilution law. On p. 298 it is stated that the Solvay process for making sodium carbonate is now being superseded by the electrolytic process (presumably Hargreaves and Bird). The reviewer knows no facts which justify such a statement. *Wilder. D. Bancroft.*

The Chemistry of the Diazo-Compounds. *By John Cannell Cain. 14 x 22 cm; pp. x + 172. London: Edward Arnold. New York: Longmans, Green & Co., 1908. Price: $3.00 net.*—This is a much-needed monograph. The question of the constitution of the diazo compounds is one over which organic chemists have fought for many years with ever-changing views. A summarized statement of our knowledge in regard to these compounds is therefore much to be desired and this we now have. The author has been handicapped a little by trying to do two different things, to give the chemistry of the diazo compounds and to sketch the development of the constitution formulas. While the author has given us a very interesting account of the conflict between Hantzsch and Bamberger, it must be admitted that the narrative is a bit jerky and disconnected in places. This may perhaps be due in part to the fact that the author does not agree with either side and is waiting a chance to bring in his own theory, which he does in an appendix. His view is that in the diazo salts we have a quinonoid configuration of the diazo-salts and "that an atom of nitrogen in these salts is attached to the aromatic nucleus by two linkings."

Wilder D. Bancroft.

Les Découvertes Modernes en Physique. *Leur Théorie et leur Rôle dans l'Hypothèse de la Constitution Électrique de la Matière. By O. Manville. 14 x 22 cm; pp. ii + 186. Paris: A. Hermann, 1908. Price: paper, 5 francs.*—The author feels that the electronic theory of matter has not received the attention in France that it should, chiefly because of the lack of a suitable book on the subject. It is the praiseworthy object of the author to dispel these clouds of ignorance. The treatise under consideration contains seven chapters: electrical discharge through liquids; discharge through gases; ionization of gases; electrons; introduction to the electronic theory of matter; induced radio-activity; the electronic theory of matter.

The first chapter deals with the electrolytic dissociation theory. The author ascribes to Arrhenius the famous saying that electrolytes are salts. He considers that the ions are the elements existing in the solutions with free affinities. A necessary consequence of this is that the ions must polymerize when they are set free. This presents no difficulty with hydrogen and chlorine. Some people might have difficulties with copper; but the author states boldly that metallic copper is a solid polymer of the copper ion. Incidentally, the author gives the Greek words from which ion, anion, cation, anode and cathode are derived; but either his Greek is faulty or his proof-reading because the accents are wrong on every one of the words involved. As a rule, the author does not mis-spell foreign names with that grace which usually characterizes French writers, though it must be admitted that Hittdorf and Towsend are pretty successful efforts in this line.

It is possible that the author's book will have the desired effect upon his countrymen. If so, he will have been successful even beyond his deserts.

Wilder D. Bancroft.

Radioaktive Umwandlungen. *By E. Rutherford. Übersetzt von M. Levin. (Die Wissenschaft. Sammlung naturwissenschaftlicher und mathematischer Monographien. Heft 21.) 14 x 21 cm; pp. vii + 285. Braunschweig: Friedrich Vieweg und Sohn, 1907. Price: paper, 8.00 marks; linen, 8.60 marks.*—The English version has already been reviewed (11, 423). It is a pleasure to note the appearance of a German translation. *Wilder D. Bancroft.*

Flüssige Kristalle und die Theorien des Lebens. *By O. Lehmann. Zweite durch Zusätze verbesserte Auflage. 13 x 20 cm; pp. 69. Leipzig: Johann Ambrosius Barth, 1908. Price: linen, 1.50 marks.*—The first edition of this little book appeared in 1906 and was reviewed (11, 640). One interesting feature of the new edition is the quotation on p. 68 of several of the reviews of the first edition from which it appears that there is great difference of opinion as to what the author's view-point really is. The author himself says that while he is striving toward the artificial production of living organisms, he does not assume that such a result is necessarily possible. He is trying to find out whether there are reasons which make such a result impossible and, if so, what they are. *Wilder D. Bancroft.*

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