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CONTENTS OF VOLUME XVIII

1. JANUARY

2. FEBRUARY

3. MARCH

4. APRIL

5. MAY

6. JUNE

7. OCTOBER

8. NOVEMBER

9. DECEMBER

THE THEORY OF DYEING. I

BY WILDER D. BANCROFT

It is generally admitted that no adequate theory of dyeing has yet been presented, and yet it seems to me that there are sufficient data to enable the outlining of a satisfactory theory; in fact we have reached a point where such a theory is essential as a guide to research work.

There are a number of points to be accounted for. Some color baths will dye wool or silk fast to washing and will not act the same way with cotton, while other baths will dye cotton direct. The addition of sodium sulphate to a bath may cause the fiber to take up more or less color than it otherwise would. In some cases an acid bath promotes dyeing; in other cases it checks it. Treatment of cotton with salts of aluminum, chromium, tin, iron, etc., will cause the dyeing of the fiber by color baths which ordinarily will not act in this way. The addition of tannin will cause other colors to be taken up by cotton. The color is fixed more thoroughly if sodium arsenate is added to an iron mordant, sodium phosphate to an alumina mordant, tartar emetic to a tannin mordant, etc.

Since the dye is apparently soluble in aqueous solution, and since it does not wash out of the fiber, the simplest way of accounting for this is to postulate the formation of an insoluble compound and this assumption is made explicitly by all, or nearly all, of the people who are familiar with the practical side of dyeing. On the other hand, this assumption has not proved a satisfactory working hypothesis. A hundred years of it has left us with the feeling that dyeing is essentially a mysterious process. Consequently, those of us who have no technical knowledge, but who have to lecture on the subject, incline very strongly to the belief that we are dealing with adsorption, and that definite chemical compounds are not formed as a rule though they may be in certain special cases.

If we are to assume the formation of definite chemical compounds, we must assume that wool, cotton, and charcoal may each act either as a base or as an acid. This hypothesis might be permissible in the case of wool; but it is a questionable one for cotton and an absurd one for charcoal. Of course one does not usually speak of dyeing charcoal; but charcoal takes up dyes quite as readily as wool or silk, and more readily than cotton. The color of the dye does not show against the black background; but that does not affect the principle involved. Fortunately, the whole question is not one of personal preference or of any so-called chemical intuition; it is a matter to be decided by quantitative analysis. If the dye forms a sparingly soluble compound with the fiber, we shall have the unchanged fiber and the fiber-dye compound as two separate phases, and consequently a constant concentration in the dye-bath until the fiber has been converted completely into the fiber-dye compound, when the concentration of the dye in the bath will vary while the concentration of the dye in the fiber will remain constant. If we have a case of adsorption, the concentrations of the dye in the fiber and in the bath will vary continuously.

Since the behavior of wool with acid or alkali has been put forward as proving the basic or acid nature of the fiber, we will begin by applying our test in the case of acids, alkalies and salts before taking up the special cases of dyes.

Pelet-Jolivet[1] gives data for wool with caustic soda and sulphuric acid (Tables I and II).

TABLE I

5 grams wool, 500 cc solution, 3 days, cold

Total NaOH Milligrams	Adsorbed NaOH Milligrams	Dissolved NaOH Milligrams
100	67.5	32.5
200	140	60
400	305	95
600	480	120
800	655	145

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[1] "Die Theorie des Färbeprozesses," 77, 78 (1910).

TABLE II

1 gram wool, 150 cc solution, 2 days, temperature 20°

Total H_2SO_4 Grams	Absorbed H_2SO_4 Grams	Dissolved H_2SO_4 Grams
0.126	0.051 (0.054)[1]	0.075
0.252	0.057 (0.055)	0.195
0.378	0.060 (0.060)	0.318
0.504	0.066 (0.060)	0.438
0.630	0.076 (0.070)	0.554
0.757	0.076 (0.075)	0.681
0.883	0.080 (0.080)	0.803
1.009	0.095 (0.085)	0.914
1.135	0.088 (0.085)	1.047
1.261	0.091 (0.090)	1.170

No matter what corrections one makes for experimental error, there is absolutely no evidence that wool forms a definite compound either with caustic soda or with sulphuric acid. Gelmo and Suida[2] found that different samples of wool took up different quantities of sulphuric acid or of hydrochloric acid. This is what might be expected in case of adsorption; but it is hard to account for on the basis of a definite compound unless we assume that one sample of wool was more alkaline than the other. This cannot have been so, because the wool which took up the smaller amount of sulphuric acid also took up less ammonia than the other sample. The possible variations in the case of unquestioned adsorption are brought out clearly in Table III which contains data by Pelet-Jolivet[3] for the action of different commercial charcoals on solutions of methylene blue and of crystal ponceau.

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[1] The numbers in parentheses are the ones actually given. The others are the ones which balance.

[2] Monatsheft für Chemie, 25, 863 (1905); 26, 225 (1906).

[3] "Die Theorie des Färbeprozesses," 58 (1910).

TABLE III

Description and brand	Grams of dye adsorbed per 100 g organic matter in charcoal	
	Methylene blue	Crystal ponceau
Blood charcoal, pure M	84.17	74.53
Animal charcoal, pure M	48.97	46.59
Bone black K	20.22	12.05
Blood charcoal, H	11.99	11.24
Blood charcoal, K	3.42	4.90
Wood charcoal, powdered	1.69	2.24
Soot	1.72	1.85

In another experiment[1] a granulated charcoal took up 7.8 percent methylene blue, but 8.2 percent when powdered very fine. The experiments of Walker and Appleyard[2] show that no definite compounds are formed when silk is shaken with aqueous solutions of organic acids. There is also no evidence of any compound being formed when wool is shaken with water and varying amounts of tannin (Table IV).[3] More tannin is taken up at the higher temperature than at the lower temperature, but that is the only difference.

TABLE IV

2 grams wool, 100 cc solution, temperature 18°

Total tannin Grams	Adsorbed tannin Grams	Dissolved tannin Grams
0.100	0.0234	0.0765
0.200	0.0385	0.1615
0.300	0.0484	0.2516
0.400	0.0532	0.3468
0.500	0.0585	0.4415

2 grams wool, 100 cc solution, temperature 85°

Total tannin Grams	Adsorbed tannin Grams	Dissolved tannin Grams
0.100	0.035	0.065
0.200	0.057	0.143
0.300	0.077	0.223
0.400	0.100	0.300
0.500	0.122	0.377

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[1] Pelet-Jolivet: "Die Theorie des Färbeprozesses," 68 (1910).

[2] Jour. Chem. Soc., 69, 1334 (1896).

[3] Pelet-Jolivet: "Die Theorie des Färbeprozesses," 79 (1910).

Sanin[1] has made more experiments on the amount of tannin taken up by cotton (Table V). There is no evidence of any compound being formed.

TABLE V

Tannin per 100 cc solution Grams	Tannin per gram cotton Grams	Tannin per 100 cc solution Grams	Tannin per gram cotton Grams
4.580	0.330	0.705	0.087
3.650	0.281	0.525	0.077
2.730	0.221	0.345	0.053
1.806	0.163	0.167	0.033
0.885	0.105	0.080	0.021

Mills and Takamine[2] found that wool adsorbed hydrochloric acid and caustic soda in the molecular ratio $2HCl : 3NaOH$ when treated with dilute equivalent solutions. With silk the ratio was $3HCl : 10NaOH$. For tenth-normal hydrochloric acid and ammonia Gelmo and Suida[3] find the ratio of approximately $2HCl : 1\ NH_3$ for wool and of $1HCl : 6.4\ NH_3$ for silk. This in itself shows that the effect is specific and is not a matter solely of alkalinity or acidity.

If a fiber or any other substance adsorbs a base more strongly than an acid, there will be a tendency to hydrolyze the salt of that base and that acid, the base being then adsorbed to a greater extent than the acid. Theoretically, there is always some hydrolysis in the case of sodium chloride and water according to the equation,

$$Na^{\cdot} + Cl' + H_2O \rightleftarrows Na^{\cdot} + OH' + H^{\cdot} + Cl',$$

but this reaction does not run far because caustic soda and hydrochloric acid are strong electrolytes and we cannot have a high simultaneous concentration of hydrogen as ion and hydroxyl as ion. If the caustic soda is removed, the hydrolysis can go on farther. We thus see that a neutral solution will become acid if shaken with a substance, which adsorbs the

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[1] Zeit. Kolloidchemie, 10, 82 (1912).

[2] Jour. Chem. Soc., 43, 153 (1883).

[3] Monatsheft für Chemie, 25, 863 (1905); 26, 225 (1906).

base much more strongly than the acid, that it will become alkaline if the substance adsorbs the acid much more strongly than the base, and that it will remain neutral in case the solution does not adsorb either base or acid at all or in case it adsorbs the two in practically equivalent amounts. All these cases are known and the results do not depend upon any hypothetical acidity or alkalinity of the adsorbing substance.

If fuller's earth be shaken with water and then filtered, the filtrate is neutral to litmus paper[1] or to phenolphthalein, showing that no soluble acid or base is present. If fuller's earth be shaken with a sodium chloride solution and filtered, the filtrate is acid to litmus paper or to phenolphthalein. This is because fuller's earth has adsorbed the base. If one presses litmus paper against moistened fuller's earth, the litmus paper turns red, and if one adds fuller's earth to a faintly alkaline solution of phenolphthalein the red color disappears. This is not because the fuller's earth is acid, but because it takes the base from the sodium chloride, the litmus or the phenolphthalein. This may seem like a difference between tweedledum and tweedledee; but even that is sometimes important. It is easy enough to illustrate the difference. Suppose I have an unknown but equal number of red and of yellow bananas spread out on a table. By arranging them alternately it is easy enough to see that there are an equal number of each without actually counting them. Suppose that, after an absence from the room, I notice there are more yellow bananas than red ones. It may be that some one has presented me with a number of yellow ones. It may also be that some one has carried off a number of red bananas. On either hypothesis I shall have more yellow bananas than red ones; but there is a marked difference between having bananas—or anything else—given to one and having them stolen from one.

Animal charcoal behaves like fuller's earth, though it

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[1] Cameron: Jour. Phys. Chem., 14, 400 (1910).

is less active.[1] Sodium chloride is said not to be decomposed, but sodium acetate and disodium phosphate are. We get adsorption of the acid by hydrous ferric oxide or cupric oxide. We usually write the reaction between copper sulphate and sodium hydroxide

$$CuSO_4 + 2NaOH = CuO_2H_2 + Na_2SO_4$$

but the solution is alkaline as a matter of fact. Calcium chloride and barium chloride are adsorbed practically without change by boneblack, and the sodium salt of benzopurpurine by cotton.

It is quite conceivable that the adsorption curves for an alkali and an acid might intersect, in which case the base would be taken up to a greater extent than the acid at one concentration, while the reverse would be true at another concentration. This case seems to occur with alum. Schwalbe[2] says that wool takes up more sulphuric acid than alumina from a dilute alum solution, all the sulphuric acid being taken out of a 5 percent alum. solution. From concentrated solutions wool takes up more alumina than acid. According to von Georgievics alumina and sulphuric acid are taken up in equivalent quantities from a 24 percent solution of alum while relatively more sulphuric acid is taken up from a more concentrated solution.[3] It is not clear whether these two sets of statements are contradictory or whether there are two concentrations for which alumina and sulphuric acid are taken up in equivalent quantities. In case a salt is decomposed and the basic radical adsorbed more than the acid radical, washing the fiber will take out relatively more acid than base.[4]

It is now clear that no definite compounds are formed when wool, silk or cotton is shaken with aqueous solutions of acids, bases or salts, and that we are dealing throughout

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[1] Liebermann: Akad. Wiss. Wien, 74, 331 (1878).

[2] Ahrensche Sammlung chemischer Vorträge, 12, 163 (1907).

[3] Cf. Dreaper: "Chemistry and Physics of Dyeing," 62 (1906).

[4] Cf. Schwalbe: Ahrensche Sammlung chemischer Vorträge, 12, 167 (1907).

with cases of adsorption. The evidence is equally strong with dyes.

Georgievics[1] dyed silk with indigo carmine, and cellulose with methylene blue. In both cases the concentrations in the dye-bath and in the fiber varied simultaneously. Pelet-Jolivet[2] gives data by himself and by others to show the same thing for methylene blue, crystal violet, safranine, crystal ponceau, and patent blue with wool; for malachite green, new magenta, eosine, and patent blue with silk; and for crystal violet, benzazurine, mikado yellow, benzo-brown G and benzopurpurine with cotton. The data for methylene blue, crystal violet, and safranine with wool are given in Table VI.

Table VI

A_1 = milligrams methylene blue per gram wool.
A_2 = grams methylene blue per liter solution.
B_1 = milligrams crystal violet per gram wool.
B_2 = grams crystal violet per liter solution.
C_1 = milligrams safranine per gram wool.
C_2 = grams safranine per liter solution.

A_1	A_2	B_1	B_2	C_1	C_2
32.7	0.01	40	0.80	38.6	1.14
44·0	0·34	47	1·77	43·0	5·7
47·7	1.29	50	2.75	47	10.3
53·0	2.21	54	3·73	51	14·9
53·3	3·20	58	4·71	53	19·7

The data of Freundlich and Losev[3] are very interesting; but these authors present their results in so unsatisfactory a way as to require an elaborate recalculation if the data are to be used. Freundlich and Losev conclude that dyes are taken up by wool and silk in the same way as by charcoal and that the evidence is conclusive that we are dealing with adsorption and not with a process involving the formation of definite chemical compounds. The same conclusion

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[1] Akad. Wiss. Wien, 103, II*b*, 589 (1894); 104, II*b*, 309 (1895).

[2] "Die Theorie des Färbeprozesses," 71–76 (1910).

[3] Zeit. phys. Chem., 59, 284 (1907).

follows from the experiments of Schaposchnikow[1] with cotton and a number of substantive dyes.

If we are dealing with adsorption, as seems to be the case, the process must be reversible theoretically, and it should be possible, theoretically at any rate, to wash the dye out of the fiber practically completely. There are plenty of dyes with which this can be done, methylene blue and cotton for instance; but the practical dyer says that methylene blue does not dye cotton, meaning thereby that cotton dyed with methylene blue bleeds so badly as to have no practical value. The case of a dye which does not wash out of the fiber seems therefore to present difficulties; but they are imaginary difficulties. If a fiber will take the dye out of a solution so thoroughly that the bath is completely exhausted, it follows that washing with that solution cannot extract enough dye to color the solution.[2] The process will thus apparently be irreversible though really reversible. As a matter of fact, no dye will withstand unlimited washing and it is well known that it is risky to heat dyed cloth and white goods together in the boiler. Dreaper[3] says that "a hank of cotton dyed with benzopurpurine (sodium salt) will, on prolonged boiling with a similar but undyed skein, give up its dye until an equilibrium of color is obtained on both skeins." We have confirmed this statement; but we were never able to do it in such a way that there was no tinge to the water.

The fact that a fiber may exhaust an aqueous bath completely does not necessarily imply that it will do the same with another solvent. As a matter of fact, alcohol will wash crystal violet out of wool[4] or magenta out of silk,[5] though it must be admitted that there are some points about the action of organic solvents which call for further study.[6]

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[1] Zeit. phys. Chem., **78**, 209 (1911).

[2] Freundlich: Zeit. phys. Chem., **67**, 538 (1909).

[3] "Chemistry and Physics of Dyeing," 149 (1906).

[4] Freundlich and Losev: Zeit. phys. Chem., **54**, 305 (1907).

[5] Sisley: Bull. Soc. chim. Paris, [3] **23**, 865 (1900).

[6] Cf. Walker and Appleyard: Jour. Chem. Soc., **69**, 1334 (1896); Schwalbe: Ahrensche Sammlung chemischer Vorträge, **12**, 121 (1908).

I now propose to show that the phenomena of dyeing can be accounted for satisfactorily on the single postulate that a fiber tends to adsorb everything in the solution in amounts varying with the nature, concentration, and temperature of the solution and with the nature of the fiber. This does not sound especially thrilling or novel; but it is the application to special cases which counts.

When we have a mixture of two salts in solution, the diffusate will contain an excess of the salt made up of the faster-moving cation and the faster-moving anion. In the same way metathetical reactions will take place in the solution so that the most readily adsorbed cation and the most readily adsorbed anion will be the ones chiefly taken up. Of the inorganic ions, hydrogen and hydroxyl are usually taken up the most readily. Leaving these out of account, it will pass as a first approximation to postulate that inorganic ions of higher valence are usually adsorbed more than the corresponding ones of lower valence. Since adsorption is distinctly a selective phenomena, this rule cannot be relied upon even when limited to inorganic ions. It will serve however as a guide.

When testing the theory of dyeing for wool and silk, we will begin with the so-called basic and acid dyes. A basic dye is one which contains the color in the basic radical while an acid dye contains the color in the acid radical. Among the familiar basic dyes are magenta, safranine, auramine, malachite green, methylene blue, crystal violet, and Bismarck brown. Among the familiar acid colors are croceine scarlet, crystal ponceau, naphthol yellow, acid green, and alkali blue.

In order to get the maximum adsorption of an acid dye we should have present an ion of the opposite charge which is readily adsorbed. We therefore deduce the following conclusions in regard to an acid dye:

(1) The dye is taken up most readily in an acid solution but may be taken up in a neutral or alkaline solution.

(2) A readily adsorbed anion decreases the amount of dye taken up.

(3) A readily adsorbed cation increases the amount of dye taken up.

These generalizations can easily be confirmed by tabulating some of Pelet-Jolivet's results with crystal ponceau.[1] Five grams of wool took up 44 mg of crystal ponceau from a neutral aqueous solution, 24 mg when 10 cc $N/10$ NaOH were added, and 109 mg when 8 cc $N/10$ HCl were present. Silk adsorbed 4.6 mg crystal ponceau from an alkaline solution, 8.7 mg from a neutral solution and 28.2 mg from an acid solution. In another set of experiments in which the concentration of the dye varied, the milligrams adsorbed by wool were 41.7, 62.8, 76.5 and 86.5 from a neutral solution and 65, 113, 150, and 178 from a solution containing 15 cc $N/10$ H_2SO_4 per liter. Increasing the degree of acidity increases the amount taken up, at any rate over quite a range of concentrations as is shown in Table VII. I do not know whether the decrease in the adsorption with the higher concentrations of sulphuric acid is due to the increased concentration of SO_4 ion working against the hydrogen ion or whether there is a permanent decrease in the adsorbing power of wool after the wool has been exposed to acid of this concentration. This point could easily be determined experimentally; but Pelet-Jolivet apparently did not appreciate the importance of this.

TABLE VII

3 grams wool, 200 mg crystal ponceau per 200 cc H_2O

H_2SO_4 Grams	Adsorbed dye Milligrams	H_2SO_4 Grams	Adsorbed dye Milligrams
0.0	33	3.92	174
0.015	40	7.84	178
0.049	112	15.88	(140)
0.245	137	39.2	(128)
0.784	155	—	—

In accordance with conclusion No. 2 acidifying with a bivalent acid, such as sulphuric acid, should cut down the

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[1] Pelet-Jolivet: "Die Theorie des Färbeprozesses," 94, 98, 119, 148 (1910).

amount of dye taken up much more than acidifying with an equivalent quantity of hydrochloric acid. This has been observed by Pelet-Jolivet,[1] Tables VIII–IX. Just as the theory requires, the amount of dye taken up decreases as we pass from hydrochloric acid to sulphuric acid and then to phosphoric acid. Addition of sodium sulphate cuts down the amount of dye adsorbed.

TABLE VIII

5 grams wool, 0.372 mg crystal ponceau per 200 cc solution

cc $N/10$ acid added	Milligrams crystal ponceau adsorbed		
	HCl	H_2SO_4	H_3PO_4
0	44	42	42
8	109	93	48
18	158	140	80
28	171	153	102

TABLE IX

5 grams wool, x = percent crystal ponceau, 200 cc solution

x	Milligrams crystal ponceau adsorbed		
	3 cc $N/10$ H_2SO_4	Water	0.12 g Na_2SO_4
0.1	65	41.7	36.2
0.2	113	62.8	59.8
0.3	150	76.5	64.8
0.4	178	86.5	70.8

We have rather an interesting case with potassium chloride,[2] Table X. As I interpret these results, chlorine as ion is probably adsorbed somewhat more readily than potassium and consequently the adsorption of the dye decreases with increasing salt concentration. On the other hand the potassium chloride decreases the solubility of the dye in water and in that way increases the tendency of the dye to be ad-

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[1] "Die Theorie des Färbeprozesses," 94, 119 (1910).

[2] Pelet-Jolivet: "Die Theorie des Färbeprozesses," 94, 149 (1910).

sorbed. With higher concentrations of the salt, the latter tendency is the more important and the amount of adsorbed dye passes through a minimum and then increases until the dye is actually salted out.

TABLE X

3 grams wool, 200 mg crystal ponceau per 200 cc solution

KCl Grams	Milligrams dye adsorbed	KCl Grams	Milligrams dye adsorbed
0	32	—	—
0.0075	32	0.756	43
0.0227	28	1.512	55
0.0378	28	3.024	71
0.0756	28	6.048	91
0.378	33	15.12	(100)
—	—	24.19	(50)

The truth of the conclusion that a readily adsorbed cation increases the adsorption is shown in Table XI.[1] We see from

TABLE XI

Wool, effect of cations[2]

Dye solution	Conc.	Mgm dye adsorbed
Free acid of crystal ponceau	$N/100$	290
Na salt of crystal ponceau	$N/100$	65
Na salt of crystal ponceau	$N/500$	30
Mg salt of crystal ponceau	$N/500$	45
Free acid of crystal ponceau	$N/100$	138
Al salt of crystal ponceau	$N/100$	159
Free acid of crystal ponceau	$N/500$	14
Mg salt of crystal ponceau	$N/500$	7.8
Al salt of crystal ponceau	$N/500$	14.6
Free acid of naphthol yellow	$N/100$	205
Na salt of naphthol yellow	$N/100$	35
Mg salt of naphthol yellow	$N/100$	70

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[1] Pelet-Jolivet: "Die Theorie des Färbeprozesses," 97, 108.

[2] The different series in this table are not comparable.

these figures that the amount of adsorbed dye decreases with decreasing adsorption of the cation, so that we have Al > Mg > Na.

Since sodium as ion has a relatively slight effect on the adsorption and sulphate as ion a relatively large one, it follows that sodium sulphate will cut down the adsorption of an acid dye and will tend to strip an acid dye which has already been adsorbed. This is a perfectly familiar phenomenon. Sodium sulphate is often added to the bath to act as a leveller. While a strongly acid bath would cause the most dye to be taken up, the dye would be adsorbed so rapidly that there would be great danger of the color not being even. For this reason, acid colors which do not readily dye even are used in weakly acid baths containing sodium sulphate, so that the dyeing shall take place more slowly and more evenly though not to so deep a shade. In case of uneven dyeing, the sodium sulphate will strip the excess color. In regard to dyeing with acid colors, Knecht[1] says: "The addition of sodium sulphate to the dye-bath exerts a restraining action; the dyeing proceeds more slowly and regularly, and a more equal distribution and absorption of coloring matter takes place. Other devices to obtain even colors are the use of old dye-liquors, a diminished amount of acid, the employment of weaker acids, *e. g.*, acetic or formic acid or ammonium acetate, and the entering of the material at a low temperature."

From our present point of view, there are no longer any difficulties in the paper on "The Theory of the Acid Dye-bath" by A. W. Hallitt[2] from which I quote, because this paper is referred to so often.

"This experiment shows that sulphate of soda acts in the same way in producing evenness, and in extracting colors from the yarn, whether it is used in the bath with the acid and color, or whether the dyed yarn is treated subsequently in a separate bath of sulphate only. The bisulphate theory

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[1] Encyclopedia Britannica, eleventh edition, "Art. Dyeing."

[2] Jour. Soc. Dyers, 15, 31 (1899).

has no explanation to give of these results. They indicate that the levelling influence of the sulphate does not depend on a mere retardation of the dyeing process, but on the setting up of an opposite stripping action. If the dyeing has begun unevenly, the sulphate will strip more energetically from the darker parts of the material, and the dyeing will be more active on the lighter parts, and when the dyeing has proceeded so far that the stripping takes place as fast as the dyeing, effective dyeing will cease, but the levelling process will continue. This stripping and redyeing action is more rapid at the boil, and so we find that although most of these colors can be fixed considerably below the boil, the higher temperature is necessary to make the colors even.

"Here is another point in which the bisulphate theory fails. It is said that chloride of sodium and other neutral salts would not act in the same way as the sulphate. It is true that the chloride will not act in the same degree as the sulphate, but that in a lesser degree it acts in the same manner is shown in the following experiments:

"Two hanks were dyed with 1 percent Palatine Red A.

(*a*) With 3 percent sulphuric acid only.

(*b*) With 3 percent sulphuric acid and 50 percent sodium chloride.

(*b*) is distinctly more even than (*a*). Color left in bath, (*a*) 1.4 percent, (*b*) 6.0 percent of color used."

According to the theory presented, every adsorbable anion cuts down the degree of adsorption of an acid color. The difference between sodium chloride and sodium sulphate is due merely to the greater adsorption of sulphate. If chlorine as ion is adsorbed more than sodium as ion—which appears to be the case—a high concentration of sodium chloride should be equivalent to a low concentration of sodium sulphate, which is what Hallitt found. It must be remembered, however, that this equivalence holds only for the conditions under discussion. It might easily happen that a high concentration of sodium chloride had a different effect on the solubility of the dye from that exerted by a low concentration of sodium sulphate. In that case this would be a disturbing factor.

On another page of the same paper Hallitt[1] says:

"The concordance which is found in the figures for the color left in the dye-bath, and extracted from the yarn, when the experiments are carried on under exactly similar conditions shows that at the end of the dyeing process, a definite state of equilibrium is arrived at. The opposite forces composing this equilibrium are on the one hand the attraction that exists between the color and the fiber, and on the other hand the solvent action of the exhausted dye liquor on the color already fixed on the yarn. As the yarn is gradually loaded with color its attraction grows less, and as the dye liquor is exhausted its solvent action becomes greater. A point is therefore arrived at, where these two opposite processes have the same velocity and are in equilibrium. But we find that this point of primary equilibrium (as we may call it) between the yarn and the dye liquor is a movable one. Thus, by the addition of acid it is moved in favor of the yarn, and by the addition of sulphate of soda it is moved in favor of the bath. It varies also with different colors."

The theory, which I am presenting, calls for reversible adsorption, for an increased adsorption in presence of hydrogen as ion, and for a decreased adsorption in presence of sulphate as ion. Since the adsorption is specific, the degree of exhaustion for a given acidity will vary with the specified degree of adsorption of the acid color, which is just what Hallitt requires.

On page 34 of his paper Hallitt says: "An acid color is a salt in which the color acid needs to be liberated before the dyeing can take place.[2] Instead of our previous example of hydrochloric acid and sulphate of soda, let us now consider a solution of a color salt and sulphuric acid. The only base in the solution will be the soda base introduced in combination

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[1] Jour. Soc. Dyers, 15, 33 (1899).

[2] [This is an unfortunate definition. W. D. B.]

with the color acid. For this base both acids will compete, and the proportion falling to each will depend on their respective intensities and concentration. On introducing yarn into this solution both color acid and sulphuric acid are partially absorbed and neutralized;[1] but the color acid in larger proportion, therefore the balance is disturbed in favor of sulphuric acid; the direct change between the sulphuric acid and the color salt therefore proceeds a step further, more sulphate of soda being formed and more color set free, and absorbed by the yarn. Thus the process would go on to practical completion except that the color acid, though absorbed by the wool, is not removed entirely from the field of action, but is subject to the solvent action of the exhausted dye-liquor. The solvent action is very slight with many of the color acids, but considerable with some; and in either case it finally establishes an equilibrium with the enfeebled dyeing action. I said that the rapidity with which the color acid would be liberated would depend on the concentrations and intensities of the two acids.

"With regard to the intensity of the color acid, is it not well known that those colors that dye the most evenly and exhaust the bath the least have strong acid elements, such as the nitro and highly sulphonated colors, thus enabling them to resist rapid displacement by the sulphuric acid. In saying this, I do not overlook the fact that each type of color has its own individuality. We know hardly anything of the nature of the compounds formed between the color acids and the basic elements of the wool fiber; but it may safely be assumed that some of these color acids form more soluble compounds than others, and this being so will dye more evenly by stripping more readily. But with reference to the intensity of the color acid, we may say this, that colors of the same family are made more even-dyeing by an increase in the intensity of the acid element of the color. That is all that the laws of the equilibrium would require.

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[1] [It would have been safer to have omitted the words "and neutralized." W. D. B.]

"If I may take it as an accepted fact that a color dyes more slowly and evenly as its acid intensity is increased (and there are, no doubt, some of you who are familiar with the preparation and chemistry of these colors, and who will correct or confirm me in this), then this seems to me a fact of the greatest theoretical importance. For if the reaction of the color salt were primarily and directly with the yarn, then we should expect that the stronger the acid element in the salt the more active would be its attack on the yarn, and the more uneven its dyeing properties. But this is the opposite of the facts. But on the view that the color acid can only dye as it is displaced from its soda base, and that this displacement follows the laws of equilibrium already stated, then the relation is natural which is known to exist between the intensity of the color acid and its even dyeing and imperfectly exhausting character. That is to say, that the more intense color acid would be liberated more slowly from its base, and the dyeing being thus more gradual, would not go on so far before being met and balanced by the solvent action of the dye-liquor on the fixed color."

The weak point in this discussion—apart from phraseology—is that Hallitt does not take into account the effect that the adsorption of the sulphate radical has on the adsorption of the color acid. For any given color acid we must consider both the acidity of the solution and the effect of the nature of the acid if we are to understand the way things go. Hallitt ignored the effect due to the anion and consequently got into trouble, as the following paragraphs show:

"The influence of the mass of the sulphuric acid was shown by Dr. Knecht[1] in a communication......, according to which a quantity of sulphuric acid equivalent only to the color salt in solution dyed a very weak shade, and ten to fifteen times that quantity was required to give a full shade. A large part of this excess is neutralized by the wool, but still it appears that a certain preponderance of mass of the acid

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[1] Jour. Soc. Dyers, 14, 107 (1888).

is necessary to carry the direct change far enough for practical dyeing purposes.

"Now, with regard to the intensity of the assistant acid, every one knows that colors that dye unevenly with sulphuric acid may be dyed more evenly with acetic acid. As the latter has only about 1-16th the intensity of sulphuric acid its action in enfeebling the direct change is what the law would indicate.

"On this subject I find the following in the admirable manual of their colors (A., General part, 1896) issued by the Farbwerke Hoechst. After an excellent paragraph in which the levelling influence of sulphate of soda is ascribed to its solvent action on the fixed color, there follows on page 64 a paragraph on the use of weaker acids for the promotion of evenness, in which it is stated that 'for uneven colors weaker acids should be employed, such as hydrochloric, oxalic, or acetic.' I assume that equivalent quantities are meant; they are not otherwise comparable. Referring to the list of intensities given we see that hydrochloric is twice as strong as sulphuric, and would not therefore be expected to dye more evenly. Oxalic is only half as strong as sulphuric, but experiment shows that for this purpose it acts more powerfully and therefore dyes less evenly. Acetic acid is the only one left, as it is the only one in general use for the purpose.

"I have made the following experiments with equivalent quantities of good *commercial* samples of these acids. Three colors were dyed in 1 percent shades, and the figures given show the percentage left in the bath, of the color used. The degree of evenness is found to be proportional to the amount of color left in the bath.

Dyed with	Palatine Red Percent	Acid Blue IV Percent	Tartrazine Percent
a. 6.84 percent hydrochloric	0.15	exhausted	exhausted
b. 3.66 percent oxalic	0.90	0.15	0.27
c. 3.00 percent sulphuric	1.4	0.35	0.85
d. 14.33 percent acetic	4.2	1.1	6.4

Leaving out sulphuric acid in this table we find that the other three act in the same order as their intensity figures indicate. Thus hydrochloric is the strongest, and it leaves the least color in the bath, and dyes the least evenly. Oxalic is weaker than hydrochloric and leaves more color in the bath, and dyes more evenly. Acetic is still weaker, and leaves still more color in the bath, and dyes still more evenly. But sulphuric, which by its intensity figure comes between hydrochloric and oxalic, is found in this experiment between oxalic and acetic. We see from this that sulphuric acid is anomalous. It acts less intensely in the bath than its figure indicates. This led me to make the following experiment, in which the amount of acid used is obtained by multiplying the equivalent figures used in the last experiment by numbers which are inversely proportional to the intensities. We thus obtain quantities of acid which represent equal intensities. A bath was made of 1 percent Palatine Red in each case, and the percentage of this left in the bath in each case is shown.

(*a*) 6.84 percent hydrochloric, color left in bath 0.13 percent of color used.

(*b*) 15.26 percent oxalic, color left in bath 0.15 percent of color used.

(*c*) 6.12 percent sulphuric, color left in bath 0.90 percent of color used.

(*d*) 47.76 percent acetic, color left in bath 0.15 percent of color used.

In this experiment hydrochloric, oxalic, and acetic acids exhaust equally, and the hanks are equally uneven, while sulphuric exhausts considerably less, and the hank is considerably less uneven.

"This experiment and the preceding one indicate two things:

"(1) That as a general law the even-dyeing quality of an acid is proportional to its acidic intensity, and (2) that there is something abnormal in the action of sulphuric acid which causes it to act less energetically and to dye more evenly than its intensity figure indicates. What is the cause of this behavior of sulphuric acid?

"It has been shown by Dr. Knecht that when wool is boiled with hydrochloric and sulphuric acids separately, the amount of sulphuric acid neutralized by the process is much greater than by hydrochloric.[1] This tends to explain the matter, for if the free sulphuric acid is neutralized more than the other acids it will act less intensely by reason of its diminished mass. The following experiment was made:

"Four baths were prepared with the following equivalent quantities of the four commercial acids: Each bath was tested with caustic potash solution and phenolphthalein. A hank was then boiled three-quarters of an hour in each bath. The yarn had been first boiled in clean water, and rinsed in hot water to free it from soap or alkali. After the three-quarters of an hour boiling each hank was lifted, well wrung, and the drainings run back into the bath. Each bath was then tested with caustic potash as before, to find what proportion of the acid remained free in the bath. The hanks were finally dyed in neutral baths of 1 percent. Palatine Red, and the proportion of the color left in the bath was determined. The following are the figures:

Percentage of acid reckoned on the weight of yarn	Proportion of the free acid left in bath after boiling	Proportion of color used, left in dyebath
a. 11.4 percent hydrochloric acid	36.4 percent	0.08
b. 6.1 percent oxalic acid	35.5 percent	0.30
c. 5.0 percent sulphuric acid	26.6 percent	0.90
d. 23.8 percent acetic acid	60.1 percent	5.25

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[1] Dr. Knecht's figures are:

	HCl Percent	H_2SO_4 Percent
Original amount of acid employed	7.94	5.00
Free acid left in solution after boiling the wool	4.83	1.40
Free acid boiled out of the wool subsequently	2.39	1.26
Acid absorbed or neutralized by wool	0.72	2.34
	7.94	5.00

See Jour. Soc. Dyers, 14, 105 (1888).

"This experiment shows that there is much less sulphuric left in the acid bath at the end of the boiling process than of hydrochloric or oxalic, and in the subsequent dyeing experiment the percentage of the color left in the dye bath by the sulphuric hank shows that much less free acid is carried away by the sulphuric hank than by the other two, otherwise its degree of exhaustion would be greater than oxalic.

"The amount of sulphuric neutralized must therefore be considerably greater than of any of the other acids tried.

"Seeing then that sulphuric acid is neutralized, when boiled with wool, to a much greater extent than the other acids tried, it is brought into line again with the law of equilibrium, and its apparently abnormal action, where it behaved less actively than the weaker oxalic acid, is explained by its greatly diminished mass owing to neutralization."

These experiments of Hallitt's show that sulphuric acid is adsorbed by wool—not neutralized—more completely than is hydrochloric acid, acetic acid or oxalic acid, and that consequently it cuts down the amount of color taken up by the wool. With hydrochloric, oxalic, and acetic acids, the degree of acidity is apparently the important factor and the effect due to adsorption does not show up strongly in these experiments though such an effect must be there and would be brought out by more careful experiments. For the case of sulphuric acid the effect due to the adsorption of the acid radical is so marked that it cannot be overlooked. Hallitt is not right, however, in saying that the 'apparently abnormal action, of behaving less actively than the weaker oxalic acid, is explained by its greatly diminished mass owing to neutralization.' While the decrease in concentration of the solution is a factor, the really important one is the increase in the concentration of sulphate in the wool."

There is another point in Hallitt's paper, p. 36, which calls for comment. "Then again, throughout this paper there runs the assumption that the color acid must be liberated before it can act on the yarn. I believe in all our thought on the subject this is taken for granted. It might be supposed to follow from this that if used in a free state the color acid would dye the wool readily. But from hasty experiments made during the last day or two from samples kindly supplied to me by Mr. Turner, of Messrs. Read Holliday and Sons, I find that without any other acid the free acids of scarlet 2R and Orange G dye very feebly indeed, in fact they give hardly more than a stain, and not quite so deep a one as the neutral color salts. The addition of 3 percent of sulphuric acid to the bath of free color acid causes the dyeing to go forward until only 1.25 percent of the color used is left in the bath; and if an equivalent quantity of hydrochloric acid is used the bath is completely exhausted. With the free color acid of Cardinal Red similar results are obtained, with the exception that in this case a better shade is dyed with the color acid only, perhaps half the color being extracted from this bath.

"This shows that the presence of free color acid in the bath is not of itself sufficient; and that the same difference between the action of sulphuric and hydrochloric acids remains when there is no color salt to decompose. This appears to emphasize the conclusion that the chief function of these assistant acids is to act directly on the wool fiber, in a way which prepares the wool to receive the acid colors. Until light is thrown on the nature of this action, I am afraid we shall not go very far in discussing the theory of acid dyeing."

It is not necessary that the color acid must be liberated before it can act on the yarn. In special cases the wool itself may hydrolyze the salt and take up the acid. In a sense it may be said that this involves the setting free of the color acid; but this is not what Hallitt meant as is shown by the fact that he says that one would expect the color acid, if used in a free state, to dye wool readily. This would be a natural belief if we were dealing with the neutralization of an acid by a base, but we are not. Adsorption is specific. One substance will be adsorbed a good deal and another only slightly. In one case wool may be able to take the color acid out of an alkaline solution; in another it may take up the color acid but slightly from an acid solution. All I have claimed is that—excluding disturbing factors—the color acid will be taken up more completely the more acid the solution and less completely the more alkaline the solution. Hallitt finds, as he should, that the free acids of Scarlet 2R and Orange G dye wool more completely when hydrochloric acid or sulphuric acid is added to the solution. He finds, as he should, that 3 percent sulphuric acid causes a less complete exhaustion of the bath than an equivalent quantity of hydrochloric acid because of the restraining effect due to the sulphate radical. The part, which I admit I do not understand, is the statement that the free acids of Scarlet 2R and Orange G do not give quite so deep a stain as the neutral color salts. There is something wrong here, possibly a difference of concentration. This will have to be looked into; but there is undoubtedly some factor, which has been overlooked by Hallitt, and which accounts for the apparent discrepancy.

In the next paper I shall take up the case of basic colors. While the same principles hold, we have the complication of the free color base being instable in many cases, and this is an important enough phenomenon to warrant special treatment.

The general results of this paper are:

1. Dyeing is in general a case of adsorption, though definite compounds may be formed in some special cases.

2. The taking up of caustic soda or of hydrochloric acid by wool is due to adsorption and not to the formation of definite compounds between the base or acid and the fiber or any constituent of the fiber.

3. In presence of a solution a fiber tends to adsorb everything in the solution in amounts varying with the nature, concentration, and temperature of the solution, and with the nature of the fiber.

4. As a first approximation, we may assume Schulze's law that wool adsorbs an inorganic ion more completely, the higher the valence of the ion. Schulze's law is not to be taken as anything more than a first approximation. It does

not apply for instance to hydrogen and hydroxyl as ions, nor to dyes.

5. Wool does adsorb sulphates more readily than chlorides or acetates.

6. The adsorption of hydrogen as ion will tend to increase the adsorption of an acid radical while the adsorption of hydroxyl as ion will tend to increase the adsorption of a basic radical.

7. From a mixed solution wool will tend to take up the most readily adsorbed cation and the most readily adsorbed anion rather than any other combination.

8. An acid dye is taken up most readily in an acid solution but may be taken up in a neutral or alkaline solution.

9. A readily adsorbed anion decreases the amount of an acid dye taken up.

10. A readily adsorbed cation increases the amount of an acid dye taken up.

11. Since the sulphate radical is adsorbed readily by wool, addition of sulphuric acid will cause less of an acid dye to be taken up by wool than addition of an equivalent quantity of hydrochloric acid or than addition of isohydric hydrochloric acid.

12. Addition of sodium sulphate to a dyebath will cut down the amount of an acid dye taken up by wool and will consequently cause more level dyeing.

13. Since chloride is adsorbed to some extent, addition of a large amount of sodium chloride will have something the same effect as adding a much smaller amount of sodium sulphate. With high concentrations of sodium chloride, solubility changes may be a disturbing factor and must be taken into account.

14. It does not follow that an acid dye will necessarily be adsorbed readily in a slightly acid solution. The amount of adsorption for a given degree of acidity will depend on the nature of the acid dye.

Cornell University

CUPRIC OXIDE JELLIES

BY L. S. FINCH

A cupric oxide jelly has been prepared by Foerster.[1] "If one adds an excess of ammonia to an aqueous solution of copper acetate and concentrates the deep blue solution on the water bath, one obtains acute-angled, beautifully violet-colored, prisms of copper acetate ammonia. There is always a precipitation of very finely divided copper oxide which, however, can easily be kept down to a minimum. If one wishes to avoid even this minimum, copper acetate should be dissolved in 93 percent alcohol and alcoholic ammonia added. When the excess alcohol is distilled off, the copper acetate ammonia crystallizes in a perfectly pure state. The salt can easily be recrystallized from strong alcohol, separating in the form of short prisms or of acute octahedra. It can be dried over sulphuric acid in a vacuum without decomposition. The composition corresponds to the formula $Cu(CH_3CO_2)_2.2NH_3$."

"Copper acetate ammonia dissolves in a very small amount of water forming a deep blue solution. If it is placed in a bell-jar over water, it deliquesces in the course of time. If a solution, prepared in either of these ways, be diluted, it sets to a light blue jelly, which changes in time to a fine powder."

The first thing to do was to duplicate Foerster's results. Copper ammonium acetate was prepared by adding ammonia to a saturated solution of copper acetate and heating very carefully on the water bath to prevent the formation of cupric oxide. This last can be prevented partially by the addition of alcohol. The desired salt crystallizes in purple octahedra which were washed with 95 percent alcohol and dried in a desiccator over concentrated sulphuric acid. They were then allowed to deliquesce over water. More water was then added and the solution shaken, whereupon a blue jelly was formed. While the upper part of the jelly looked all right, there was a precipitate in the bottom of the beaker. After

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[1] Ber. chem. Ges. Berlin, 25, 3416 (1892).

the jelly had stood for an hour or so it broke down into a light blue, gelatinous precipitate and a dark blue supernatant liquid. This method of forming a jelly was slow and difficult. So the copper ammonium acetate was washed with 95 percent alcohol and dried in the air. Water was added directly to the crystals instead of indirectly by deliquescence, and the mixture shaken. During the shaking the solution solidified to a blue jelly which was quite as good as, if not better than, the jelly obtained by Foerster's method. The jelly was not permanent and broke down, as before, into a bluish precipitate and a blue solution. When left in an open beaker the water evaporated slowly, leaving a dry residue which had the appearance, under the microscope, of small chestnut burrs. If a little water is added to the dried mass and if the mixture is then shaken, the solution sets again to a jelly which before long breaks down as before. These operations can be repeated apparently indefinitely.

Though these jellies had the merit that they could be restored by adding water to the dried mass, which was not the case with the chromic oxide jellies, they had the disadvantage of not being permanent. I tried to remove this defect by further purifying the copper ammonium acetate, by adding varying quantities of water, by keeping the jellies in a closed vessel or in a cool place. All these experiments gave negative results, though keeping the jelly in a cool place seemed to make it a trifle more stable.

Instead of adding pure water, a 0.5 percent solution of gelatine was used. This retarded the breaking down of the jelly, but did not make it permanent. Next a 10 percent sugar solution was tried. This was a distinct improvement, since a jelly made with this stayed up over night and later dried to a syrup. Even this jelly could not be called permanent.

When making the original copper ammonium acetate solution, it was noticed that the solution thickened all at once when the proper amount of ammonia was added, almost giving a jelly. It was, therefore, thought that perhaps one could make a jelly direct from a copper acetate solution. Different amounts of ammonia were added to saturated solutions of copper acetate and suspensions were obtained which approached very closely to a jelly. This was markedly the case when using a supersaturated solution of cupric acetate. Substituting a ten percent sugar solution gave a better jelly, while gelatine seemed to have a tendency to precipitate the hydrous cupric oxide. None of these suspensions or jellies were really satisfactory because a gelatinous precipitate separated in time. They were quite as permanent, however, as those formed from copper ammonium acetate. Hence the only advantage of going through the copper ammonium acetate stage is to get the correct amount of ammonia automatically.

Since manganese sulphate retards the change of the blue, hydrous cupric oxide into the black cupric oxide[1] making the former fairly stable at 100°, it was thought that perhaps this salt might have a beneficial effect on the jelly even though the difficulty here is not the formation of black oxide. A small amount of crystallized manganese sulphate was added to the copper acetate solution, which was then allowed to stand for a few minutes before the ammonia was added. It was found that the presence of manganese sulphate prevented the immediate precipitation of hydrous copper oxide and caused the slow formation of a permanent jelly. Experiments were then made to determine the best amounts of ammonia and of manganese sulphate to add. For each experiment 50 cc saturated copper acetate solution were taken. The ammonia was concentrated ammonia diluted with an equal volume of water. The data for varying amounts of ammonia are given in Table I. From the experiments in Table I it is clear that a permanent jelly is obtained only by keeping within the limits of 3–4 cc ammonia. Experiments were also made with 2.5 cc and 3.0 cc ammonia but no manganous sulphate. In each case an immediate precipitate was formed which settled on

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[1] Tommasi: Bull. Soc. chim. Paris, [2] **37**, 197 (1882); Comptes rendus, **99**, 37 (1884).

standing. In Table II are given data for varying amounts of manganous sulphate. These are not as accurate as they should be, because unfortunately care was not taken to be certain that all the manganese salt had dissolved before the ammonia was added:

TABLE I

50 cc saturated copper acetate solution; diluted ammonia (1 : 1); 1 gram crystallized manganous sulphate

NH_4OH cc	Quality of deposit
2	Light blue precipitate on standing
4	Permanent blue jelly (slight brownish tinge)
6	Gelatinous precipitate, solution brown
8	Quick-settling precipitate, solution brown
2	Light blue precipitate on standing
3	Permanent light blue jelly
4	Permanent blue jelly (slight brownish tinge)
5	Gelatinous precipitate, settles slowly
2.5	Jelly, not permanent; nearly colorless solution
3.5	Permanent light blue jelly
4.5	Jelly, not permanent; brownish solution
2.8	Jelly, not permanent
2.2	Jelly, not permanent
3.2	Permanent blue jelly
2.8	Jelly, not permanent

TABLE II

50 cc saturated copper acetate solution; 3 cc diluted ammonia (1 : 1); crystallized manganous sulphate

$MnSO_4.7H_2O$ Grams	Quality of deposit
1.0	Fair jelly
3.0	Fair jelly but settles somewhat in two days
5.0	Jelly, not permanent
10.0	Jelly, not permanent
7.0	Jelly, not permanent
4.0	Jelly, not permanent
0.5	Permanent blue jelly (excellent)
0.2	Permanent jelly but darker colored at bottom

From the experiments in Table II we see that the best results are obtained with about 0.5 gram manganous sulphate. Increasing the amount of ammonia or decreasing the amount of manganous sulphate darkens the color of the jelly.

It had been assumed that the manganese radical was the effective one in making the cupric oxide jelly permanent and consequently still better results were expected from manganous acetate. This anticipation proved ill-founded. Manganese acetate gave rise to a mushy suspension which was not a jelly. Manganese nitrate, carbonate, phosphate, and oxalate were added to the solutions and had no beneficial effect. When one gram manganous chloride was added, a very good light blue suspension was obtained but no jelly. With lower concentrations of chloride, the precipitate settled more rapidly. The sulphate is thus the only salt which causes the formation of a jelly when added to an acetate solution. The chloride prevents immediate precipitation but the suspended particles do not coalesce to form a jelly.

These experiments raised the suspicion that the manganese radical was not the important factor, in which case the sulphate radical must be. This appeared to be negatived by the fact that copper sulphate does not give a jelly when treated with ammonia. It behaves like copper nitrate or cupric chloride. It was thought a good plan to try experiments with a solution containing as few ions as possible and consequently hydrous copper oxide was formed from copper nitrate, copper sulphate, and copper acetate solutions. The different precipitates were filtered and washed as clean as possible from adsorbed material. They were then dissolved in ammonia—which does not take place readily—and the ammonia removed by means of a suction pump. No jellies were obtained, the hydrous copper oxide reprecipitating as the ammonia was removed.

The sulphate problem was therefore attacked again. The easiest way to reconcile the good effect of manganous sulphate with the fact that copper sulphate gave no jelly was to postulate that a small amount of sulphate was beneficial while a large amount was not. Adding manganous acetate and a few drops of sulphuric acid gave rise to a good jelly when ammonia was added. This differed from the earlier experiments in that the manganese and the sulphate were no longer present in equivalent quantities. I then discarded the manganese salt and added sulphuric acid in small amounts to the copper acetate solutions. The experiments were successful. On adding ammonia, good permanent jellies were obtained which were of a lighter blue than when manganese was present. When these jellies were allowed to stand for several weeks in open beakers, they dried to a powder which resembled chestnut burrs in appearance. When shaken with water a solution was formed which set to a permanent jelly. The process could be repeated once more, and probably indefinitely. The best jelly was obtained by taking 50 cc saturated copper acetate solution, four drops of concentrated sulphuric acid, and 3.5-4.0 cc diluted ammonia (1 : 1). With two drops of sulphuric acid the jelly was not permanent though (or because) it formed more rapidly than when drops of acid were used. With more than ten drops of acid, the jellies were not good. Adding hydrochloric acid instead of sulphuric acid was not successful. On the other hand, potassium sulphate gave as good a jelly as sulphuric acid.

From all this, it seemed to follow that a suitable mixture of copper acetate and copper sulphate solutions should yield a good jelly though neither of them will do so separately. I mixed 47 cc saturated copper acetate solution with 3 cc saturated copper sulphate solution and added ammonia. Duplicate experiments were made and jellies were obtained which stood up admirably for a week and then broke down suddenly. It is probable that other mixtures would have been really permanent, but there was not time enough in which to try this.

The general results of this paper are:

1. When copper ammonium acetate is shaken with water, a jelly is formed which is not permanent. If the decomposed jelly is allowed to evaporate to dryness and the residue is

shaken with water, a jelly is formed which is also not permanent. The process can apparently be repeated indefinitely.

2. When copper ammonium acetate is shaken with a ten percent sugar solution, a somewhat more stable jelly is formed.

3. It is not necessary to start with copper ammonium acetate. The same results can be obtained by adding a suitable amount of ammonia to a saturated copper acetate solution.

4. No jelly is obtained by adding ammonia to a copper sulphate, copper nitrate, or cupric chloride solution.

5. If a small amount of manganous sulphate be added to a saturated copper acetate solution, a permanent jelly is obtained on adding a suitable amount of ammonia.

6. The amount of ammonia must be kept within fairly narrow limits.

7. The jelly is darker in color with high concentrations of ammonia or low concentrations of manganous sulphate.

8. Other manganous salts do not act like the sulphate, though the chloride comes nearest to it.

9. It seems probable that the manganese radical has little or no effect in making the jellies permanent but that a low concentration of sulphate is the important thing.

10. The manganous sulphate can be replaced successfully by sulphuric acid or by potassium sulphate.

11. It did not prove possible to substitute hydrochloric acid for sulphuric acid.

12. A mixture of 47 parts of saturated copper acetate solution and 3 parts saturated copper sulphate, when treated with ammonia, gave a jelly which stood up for a week. By changing the ratio, it is probable that a permanent jelly could be obtained.

13. If a permanent jelly, containing sulphate, be allowed to dry to a powder, a permanent jelly can be regenerated by shaking the dried mass with water.

14. The best jelly was made by mixing 50 cc saturated

copper acetate, 4 drops of concentrated sulphuric acid, and 3–4 cc diluted ammonia (1 : 1).

15. It was not possible to prepare a jelly by dissolving washed hydrous cupric oxide in ammonia and removing the ammonia with a suction pump.

This investigation was suggested by Professor Bancroft and has been carried on under his supervision.

Cornell University

EXPERIMENTS ON EMULSIONS

BY F. R. NEWMAN

The object of this investigation was: to study the nature of emulsions and to identify the phases; to prepare emulsions of benzene and similar substances in water and of water in benzene, etc., determining the proper conditions for the preparation of each type of emulsion. Except when otherwise stated, all the emulsions were made up in 100 cc bottles and at ordinary temperature. In the early experiments the bottles were shaken by hand; but later the liquids were emulsified by shaking them violently in a shaking apparatus for periods of time varying from one minute to an hour and a half. The shaker was operated by a 1/8 H. P. induction motor and was so constructed and geared that two bottles at a time were shaken up and down in a vertical plane at the rate of approximately 360 complete oscillations per minute. The amplitude of the oscillations was about two inches. No experiments were made to find out the best form of shaker and consequently the results obtained apply only to the apparatus used. If a small homogenizer had been available, it is practically certain that better emulsions would have been obtained and over a wider range. Unfortunately, no such piece of apparatus is on the market.

Three methods may be used for determining which of two liquids is the external phase in an emulsion: the inspection method, the indicator method, and the drop method. Determination by inspection is unreliable and unsatisfactory, especially when the liquids are the same color. It should only be relied upon in the simplest cases. Robertson[1] has applied the indicator method to emulsions of olive oil and water, using the red dye, Soudan-III, which is insoluble in water but readily soluble in oils. "On sprinkling a few grains of Soudan III upon the surface of an emulsion of water in oil, the color spreads rapidly over the surface. If, how-

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[1] Zeit. Kolloidchemie, 7, 7 (1910).

ever, one sprinkles the Soudan III upon an emulsion of oil in water, the color remains confined to the droplets of oil with which the grains are in actual contact, since it cannot spread from them to adjacent drops throughout the intervening water."

Iodine is soluble in benzene and similar substances but insoluble in water, while methyl orange is soluble in water and insoluble in benzene. The iodine solution in benzene has a pink color while the methyl orange imparts an orange-yellow color to a water solution. Small amounts of iodine and methyl orange added to emulsions of benzene and water give a fairly satisfactory method of determining which is the external and which the internal phase. I did not find the indicator method so generally satisfactory as Robertson did and I made most use of the drop method, worked out by Mr. T. R. Briggs. This highly satisfactory method of distinguishing the phases is carried out in the following way: A small drop of an emulsion, of benzene and water for instance, is placed on a glass plate by means of a glass rod. A drop of water is placed on the drop of emulsion and the two stirred together. If the emulsified globules spread in the water, it is an emulsion of benzene in water; but if there is no spreading, it is an emulsion of water in benzene. This result can be checked by adding a drop of benzene to a drop of emulsion and stirring as before. If the globules spread, the emulsion is one of water in benzene; but if not, we have an emulsion of benzene in water. The principle involved is that one can dilute an emulsion by adding more of the external phase. This method worked admirably in all my experiments on emulsions. It has the advantage of being a general method, applicable to all emulsions.

Two methods were tried of making emulsions of benzene in water. In the first method the whole of the benzene was added at once to the mixture of water and protective colloid, and the contents of the bottle were then shaken by hand. In the second method the benzene was added a little at a time, the flask being shaken vigorously after each addition.

In the set of experiments now to be described, all the benzene was added at once. Mixtures having a total volume of 40 cc were made up in 60 cc bottles, containing 5, 10, 30, 30, 40, 50, 60, 70, 80, 90 and 95 percent of benzene by volume and 1 cc of 1 percent sodium oleate as protective colloid, the balance being water. These mixtures were shaken by hand for five minutes and then examined. In each case an emulsion of benzene in water was formed; but the different mixtures behaved differently on standing. With the 5, 10, 20, 30 and 40 percent benzene mixtures an ever-increasing amount of a creamy, emulsion layer formed and rose to the top, leaving a thin, dilute suspension of drops of benzene in water as a bottom layer. With the other mixtures there were three layers formed: a clear upper layer of benzene; then a creamy, emulsion layer, decreasing in thickness with the higher benzene concentrations; and below this the thin dilute suspension of drops of benzene in water also decreasing in amount with higher concentrations of benzene. Up to 40 percent all the benzene was emulsified; but this was not the case for 50 percent and more of benzene. The emulsions remained as described for forty-eight hours, at the end of which time an upper layer of benzene began to appear on the 30 percent and 40 percent benzene mixtures. In the course of a week a thin layer of benzene appeared on all the solutions, but did not seem to increase after that, contrary to Pickering's experiments.

The next experiments dealt with the effect of varying the concentration of sodium oleate. A run was made with 10 cc of a 1 percent sodium oleate instead of 1 cc. Instead of using a constant amount of sodium oleate, a solution was made up of 1 cc of a 1 percent sodium oleate in 23 cc water, and the required concentrations of benzene obtained by adding this solution in suitable amounts. The 40 percent benzene mixture then had the same concentration of sodium oleate as in the first run, the more dilute benzene mixtures containing more sodium oleate and the more concentrated benzene mixtures less sodium oleate than in the first run. Still another run was made by adding to benzene varying amounts of a solution consisting of 10 cc water plus 10 cc of a 1 percent sodium oleate solution. The varying concentration of sodium oleate has a relatively slight effect on the break-down point, or point where the benzene layer appeared, the change always occurring between the 40 percent and 50 percent benzene mixtures. More careful measurements showed an effect due to the concentration of the soap. Using 1 cc 1 percent sodium oleate and shaking 40 cc mixtures for one minute in 60 cc bottles, the break-down point was found to be between 45 percent and 46 percent benzene by volume. With other conditions the same, but using 10 cc 1 percent sodium oleate, the break-down point was found to lie between 46 percent and 47 percent benzene. With increasing amount of sodium oleate, the lower or water layer became more cloudy. The intermediate creamy layer in the higher benzene concentrations decreased in thickness with decreasing concentration of sodium oleate.

Some experiments were made, varying the order in which the benzene, water and soap solution were mixed; but no appreciable effect was noted. One run was made at 50°, adding 5 cc of a 1 percent sodium oleate solution; but the temperature effect seemed to be negligible within this range.

Experiments were then made to see whether the size and shape of the container had any effect. A 40 percent benzene mixture (8 cc benzene + 12 cc of a 1 percent sodium oleate solution) and a 30 percent mixture (6 cc benzene + 14 cc of a 1 percent sodium oleate solution) were placed in test-tubes and shaken by hand. The results were quite different from the preceding ones, both the 30 percent and the 40 percent mixture showing a clear, upper layer of benzene. Four 40 cc samples were now made up in 100 cc bottles as follows:

1. 50 percent benzene (20 cc benzene + 20 cc 0.1 percent soap).

2. 50 percent benzene (20 cc benzene + 20 cc 0.5 percent soap).

3. 50 percent benzene (20 cc benzene + 20 cc 1 percent soap).

4. 60 percent benzene (24 cc benzene + 16 cc 1 percent soap).

Nos. 1 and 2 showed no benzene layer and No. 4 did, these results being like those obtained with the 60 cc bottles. On the other hand there was no benzene layer with No. 3. We thus have the 30 percent benzene mixture showing a benzene layer when shaken in test-tubes, the 50 percent mixture when shaken in 60 cc bottles and the 60 percent mixture when shaken in 100 cc bottles. Under given conditions of shaking, the appearance of the emulsion may vary markedly with the size and shape of the container. This is probably nothing more than an indirect effect due to actual differences in the degree of mixing. The narrow test-tube is clearly the least satisfactory form and a given amount of liquid can obviously be shaken more thoroughly and more easily in a 100 cc flask than in a 60 cc one.

A series of runs were now made in which the benzene was added in portions and the flask shaken by hand after each addition. For convenience of reference let A denote mixtures having a creamy emulsion and a water layer below; let B denote mixtures with an upper, clear layer of benzene; and let C denote mixtures which form an apparently homogeneous emulsion with no second layer visible.

To 10 cc 1 percent sodium oleate + 10 cc H_2O in a 60 cc flask then were added successively 14, 2, 1, 1, 1, 1, and 1 cc benzene, the flask being shaken for one minute after each addition of benzene. The initial concentration was about 41 percent benzene and the final concentration about 51 percent benzene. All solutions belonged to type A. To 5 cc 1 percent soap in a 60 cc flask there were added successively, 3, 3, 3, 2, 3, 5, 5, 5, 5, and 10 cc benzene, the bottle being shaken for one minute after each addition. The first emulsion contained 37.5 percent benzene and was of type A; the last contained 89.6 percent benzene and was of type C. Several other similar runs were made, varying the amount of soap used, but this seemed to have very little effect. Decreasing the time of shaking after each addition to ten seconds also had no appreciable effect. The break-down point can evidently be displaced to above 90 percent benzene, the most important factor in raising the break-down point being to add benzene in relatively small amounts at the start.

Emulsions were next made up of type B and water was added to these little by little to see if the emulsion would change to type A. This could be done in each case; but the point at which this change occurs varies with varying conditions, and seems to be a function of more than one variable.

The experiments given in Table I were made in 60 cc bottles and the bottles were shaken by hand for one minute after each addition of benzene or water.

TABLE I

To 5 cc 1 percent sodium oleate solution

Add 8 cc benzene	61.5 percent	B
2 cc water	53.3	A
Add 12 cc benzene	70.6	B
1 cc water	66.6	A
Add 13 cc benzene	72.2	B
1 cc water	68.4	B
1 cc water	65.0	B
1 cc water	61.9	A
Add 20 cc benzene	80.0	B
1 cc water	76.9	B
1 cc water	74.1	B
1 cc water	71.4	A

When 1 cc 1 percent sodium oleate and 4 cc water were taken and 12 cc benzene added, the emulsion was still of the B type after the addition of 8 cc water (48.0 percent benzene) and only changed to the A type on adding 10 cc water (44.4% benzene). Decreasing the soap concentration seems to change the break-down point under these conditions from about 67 percent benzene to about 45 percent benzene.

Several runs were now made in 100 cc bottles. This permitted more efficient shaking and gave rise to very different results. The efficiency of emulsification was increased and also the stability of the emulsions. The final emulsions were perfectly homogeneous (type C) and showed no tendency to separate into layers in the course of several months. As has been found by others, it is best to begin with a small amount of the liquid to be emulsified; after some emulsion is formed it is possible and apparently desirable to make additions at increasing rates. The flasks were shaken for one minute after each addition. To 2 cc 5 percent sodium oleate solution there were added successively, 2, 2, 4, 6, 6, 8, 8, 8, and 10 cc benzene giving a homogeneous emulsion of benzene in water, and containing 96.4 percent benzene by volume. To 2 cc 5 percent sodium oleate solution there were added successively, 4, 4, 8, 12, 12, and 16 cc benzene, giving a homogeneous emulsion containing 96.6 percent benzene. To 2 cc 5 percent sodium oleate solution there were added successively, 4, 8, 16, and 24 cc benzene giving a homogeneous emulsion containing 96.3 percent benzene. To 2 cc 5 percent sodium oleate solution there were added successively, 4, 10, and 40 cc benzene, giving a homogeneous emulsion containing 96.4 percent benzene. The stiffness of these emulsions increased with increasing rapidity of addition of benzene, the last being the stiffest. The last portions of benzene are emulsified more rapidly than the first portions.

Since better results were obtained in a 100 cc flask than in a 60 cc flask, one run was made in a 250 cc flask. The results exceeded all expectations, the emulsion being the stiffest one obtained. To 2 cc 5 percent sodium oleate solution there were added successively, 5, 10, 15, 20, 20, 20, 20, 30, and 50 cc benzene, giving a homogeneous emulsion containing 99.0 percent benzene by volume. We have here 190 cc benzene emulsified in 2 cc of a 5 percent soap solution. To put it another way, the emulsion consists of 99 volume percent of benzene and 1 volume percent of water, with 0.05 g sodium oleate as emulsifying agent. In other words, 99 cc benzene and 1 cc water can be converted into a stiff jelly by a little over 0.05 percent by weight of sodium oleate. This is not quite as good as Pickering's famous jelly,[1] which consisted of 99 percent kerosene by volume and one percent of a one percent soap solution; but it is of the same order.

Using a 5 percent solution of hard soap instead of sodium oleate, a 99 percent benzene emulsion was obtained, shaking by hand. To 2 cc 5 percent hard soap solution there were added successively, 5, 10, 15, 20, 20, 20, 20, 30, and 50 cc benzene. The resulting homogeneous emulsion was even stiffer than that obtained with sodium oleate alone; but it did not stand up so well. In the course of four or five days, this emulsion cracked, disintegrating gradually until there were merely flocculent masses suspended in clear benzene. On the other hand, the emulsion made with sodium oleate was quite unchanged at the end of six weeks. This may give a clue to a discrepancy between Pickering's results and mine. Pickering[1] says that "once de-emulsification has started, it progresses at an increasing rate." This has not been my experience; and it is quite possible that Pickering's conclusions are not general ones, but apply merely to the particular emulsifying agent that he was using—a potash soap.

Since the character of the emulsions varied so markedly with the degree of shaking, all subsequent experiments were done with the power shaker previously referred to. The effect of prolonged shaking was then tested, the conditions of each experiment being: 1 cc 5 percent sodium oleate solution; final volume of solution, 40 cc; benzene added in portions; total time of shaking, 90 minutes. The details are given in Table II. The emulsions containing 10–70 percent benzene were all of the A type with a continuously-increasing amount of creamy emulsion at the top and a continuously-decreasing layer at the bottom, consisting of a thin dilute suspension of drops of benzene in water. There was no break-down point and no emulsions of type B with a clear layer of benzene at the top. When the concentration of benzene reached eighty

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[1] Pickering: Jour. Chem. Soc., 91, 2002 (1907).

TABLE II

Total volume, 40 cc; 1 cc 5 percent sodium oleate; total time of shaking, 90 minutes

Water, 35 cc		Water, 31 cc		Water, 27 cc	
Benzene 10 per cent added in cc	Minutes shaken	Benzene 20 per cent added in cc	Minutes shaken	Benzene 30 per cent added in cc	Minutes shaken
1	5	1	5	2	5
1	5	1	5	2	5
1	10	1	10	2	10
1	70	1	10	2	10
—	—	1	10	1	10
—	—	1	10	1	10
—	—	1	10	1	10
—	—	1	30	1	30

Water, 23 cc		Water, 19 cc		Water, 15 cc	
Benzene 40 per cent added in cc	Minutes shaken	Benzene 50 per cent added in cc	Minutes shaken	Benzene 60 per cent added in cc	minutes shaken
2	5	2	15	2	15
2	5	2	5	2	5
2	10	2	10	2	10
2	10	2	10	2	10
2	10	3	10	4	10
2	10	3	10	4	10
2	10	3	10	4	10
2	30	3	20	4	20

Water, 11 cc		Water, 7 cc	
Benzene 70 per cent added in cc	Minutes shaken	Benzene 80 per cent added in cc	Minutes shaken
3	10	4	10
3	10	4	10
3	10	4	10
3	10	4	10
4	10	4	10
4	10	4	10
4	10	4	10
4	20	4	20

percent, the lower liquid layer disappeared and we had a homogeneous emulsion of type C. Further runs were made, starting with 5 cc 5 percent sodium oleate and with 10 cc 5 percent sodium oleate. About the only difference to be observed is that the watery lower layer is more opaque the higher the concentration of sodium oleate. It was not possible to obtain homogeneous emulsions with 70 percent benzene or less, even by shaking them every few days, though this did decrease the lower liquid layer somewhat.

In an attempt to obtain homogeneous emulsions with lower benzene content, I started with 10 cc of a 97 percent solution, adding successively, 2, 2, 2, and 2 cc water, shaking for ten minutes after each addition. The final mixture (54 percent benzene) did not remain homogeneous but separated into two layers. To 10 cc of a 97 percent emulsion I added successively, 3, 3, 3, and 3 cc water, shaking for ten minutes after each addition. This mixture (44.4 percent benzene) separated into three layers (type B). To 10 cc of a 97 percent emulsion I added 10 cc of a 5 percent sodium oleate solution in 1 cc lots, shaking for 10 minutes after each addition. This mixture (48.5 percent benzene) separated into two layers (type A).

A few experiments were next made to see how the maximum amount of benzene in a homogeneous emulsion varied with varying concentrations of sodium oleate. To 1 cc 5 percent sodium oleate solution there were added successively, 1, 1, 2, 3, 5, 3, 5, 10, 10, 20, 30, 25, and 10 cc benzene. The last addition was too much, the excess of benzene separating while the emulsified mass remained apparently unchanged. We thus have a homogeneous emulsion at 99.1 percent and an inhomogeneous one at 99.2 percent benzene by volume. To 1 cc 1 percent sodium oleate solution there were added successively, 1, 1, 1, 2, 3, 10, 10, 10, and 20 cc benzene. Free benzene appeared on the last addition, the emulsion being homogeneous at 97.6 percent benzene and inhomogeneous at 98.4 percent benzene. Cutting down the amount of sodium oleate to two-fifths apparently decreases the permissible benzene content about one percent. In this last experiment we have 0.02 g sodium oleate converting about 98 cc benzene and 2 cc water into a jelly.

In emulsions of type A with a lower, watery layer, this lower layer is a homogeneous emulsion containing very little benzene. It seemed desirable, therefore, to learn something about its composition and to prepare such a watery emulsion, if possible, without any of the creamy emulsion being present. In the following experiments, Table III, I started with 5 cc 5 percent sodium oleate solution and added varying amounts of water and benzene, the total volume being kept at 40 cc:

Table III

Total volume, 40 cc; 5 cc 5 percent sodium oleate solution

Water cc	Benzene cc	Benzene Percent	Water cc	Benzene cc	Benzene Percent
33.0	2.0	5	34.6	0.4	1.0
33.4	1.6	4	34.68	0.32	0.8
33.8	1.2	3	34.8	0.2	0.5
34.2	0.8	2	—	—	—

The last mixture formed a homogeneous emulsion; but all the others separated into two layers (type A). This shows that a thin but homogeneous emulsion can be obtained for percentages of benzene running up to somewhere between 0.5 and 0.8 percent benzene, whereas two layers formed for concentrations of 0.8 percent benzene and higher. At the other end of the scale, homogeneous emulsions can be formed when the concentration of benzene exceeds about 80 percent, but no homogeneous emulsions were obtained with the intermediate concentrations. This had not been foreseen at all; but the explanation is easy to find.

Theoretically, it must be possible to form homogeneous emulsions with practically any volume percentage of benzene and the trouble must be with the shaking. Unless the globules of emulsified benzene are very small, the Brownian movements will not be sufficient to keep the drops distributed uniformly throughout the liquid. The larger globules will rise to the surface, forming a creamy upper layer. The emulsion will consist apparently of this layer alone when the water layer is present only in the pores. People have calculated that spherical globules will touch when they occupy 74 percent[1] of the total volume. One might reasonably expect some dripping until a somewhat higher concentration is reached, and the limiting value of about 80 percent benzene by volume, as shown by my experiments, is about what one might have expected. With more efficient emulsifying nothing of this sort will take place and we shall have a continuous series of homogeneous emulsions, which will be very fluid at the low benzene concentrations and which will become more viscous with increasing benzene concentration. My own work with the power shaker shows that the appearance of an upper benzene layer, at any rate, at concentrations below 98 percent benzene, is merely the result of insufficient emulsification.

When a homogeneous 95 percent benzene emulsion was frozen and thawed, the emulsion cracked and the change was apparently irreversible, for the emulsion could not be restored by shaking. The cracking of the emulsion is due to the rupturing of the soap films around the globules. The irreversibility is probably only apparent, and due to the coagulated sodium oleate not redissolving readily in water.

No emulsions of water in benzene were obtained with sodium oleate as emulsifying agent. Some experiments were also made with other lyophile colloids, such as haemoglobin, lacmoid, pepsin, peptone, dextrin, etc. These all gave emulsions of benzene in water and seemed not to bring out anything new. Before going on with experiments to prepare emulsions of water in benzene I decided to try some experiments with olive oil and water, because Robertson[2] had apparently obtained emulsions of water in oil as well as of oil in water by adding caustic soda. In the first run, Table IV, 1 cc of 2.5*N* NaOH was added in each case and varying amounts

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[1] Wa. Ostwald: Zeit. Kolloidchemie, 6, 108; 7, 64 (1910).

[2] Zeit. Kolloidchemie, 7, 7 (1910).

TABLE IV

Total volume, 50 cc; 1 cc·2.5 *N* NaOH; time of shaking, 10 minutes

Oil per cent	Oil cc	Water cc	Oil per cent	Oil cc	Water cc
98	49	—	20	10	39
96	48	1	10	5	44
92	46	3	5	2.5	46.5
90	45	4	3	1.5	47.5
88	44	7	1	0.5	48.5
50	25	24	—	—	—

of oil and water, the total volume being always 50 cc. The flasks held 100 cc and the mixtures were shaken for 10 minutes in the power shaker. The mixture containing 0.5 percent oil was a fluid emulsion of oil in water and the one percent mixture showed traces only of a creamy emulsion. Mixtures containing 3–50 percent oil were of the type called A, with an increasing amount of a creamy emulsion of oil in water. At 88 percent and 90 percent oil we have a homogeneous creamy emulsion of oil in water. At 92 percent we apparently get four layers, a narrow yellow upper layer which has the appearance of being a foam of air in oil; a yellow almost clear liquid, which is what Robertson called an emulsion of water in oil; the creamy emulsion of oil in water; and the thin emulsion of oil in water which forms the lower layer in the emulsions containing 3–50 percent oil. This layer has disappeared entirely in the 96 percent emulsion and the creamy emulsion disappears in the 98 percent mixture, leaving only the foam and the so-called emulsion of water in oil. Further experiments convinced me that we get no emulsions of water in oil with caustic soda as emulsifying agent. What Robertson thought was an emulsion of water in oil is merely a cracked emulsion in which the appearance of the oil is changed by the presence of solid sodium oleate, etc. When pure oil is shaken with solid sodium oleate, we get about the same appearance. Robertson's test with Soudan III proves nothing because it is not denied that oil is the external phase. It is merely denied that we have here an emulsion at all, in the sense of a coated drop of one liquid suspended in another liquid.

Another run was made with 1 cc 0.5 *N* NaOH. The general result was the same; but the 94 percent mixture formed a homogeneous creamy emulsion instead of the 88–90 percent mixtures, and there were three layers (type B) in the 90 percent and the 96 percent mixtures. With 3 cc 5 percent sodium oleate the homogeneous, creamy emulsions contained 80–86 percent oil. With 5 cc 5 percent hard soap the results were identical with those obtained with sodium oleate except that the homogeneous emulsions were a little stiffer and that there was more foaming with the lower oil concentrations.

Starting with 2 cc olive oil and 2 cc 5 percent sodium oleate, it was possible to get homogeneous emulsions varying from 76 percent oil up to 96.8 percent oil by adding oil, portions at a time and at different rates. Starting with 1 cc oil and 1 cc 5 percent sodium oleate, a homogeneous emulsion was obtained containing 99.3 percent oil. Heating mixtures before shaking seemed to have no effect other than to increase the amount of foaming. If I were arranging the emulsifiers in the order of efficiency, I should put hard soap first, then sodium oleate, with sodium hydroxide last.

Having shown that no water in oil emulsions are formed with hard soap, sodium oleate, or caustic soda, I came back to the problem of emulsifying water in benzene. To obtain emulsions of benzene in water, protective colloids were used which were soluble in water only. Consequently, it was necessary to use colloids which were soluble in benzene and insoluble in water, if one wished to emulsify water in benzene. Some of the colloids tried were: crude rubber (0.2 percent sol.); paraffin (2 percent); rosin (5 gram per 100 cc); sulphur (concentrated sol.); solutions of various resins: lard; butter; oleic acid. In nearly every case it was evident that there was a tendency to form emulsions of water in benzene; but the emulsions were very instable and cracked soon, so that something better had to be found.

Soaps of magnesium, zinc, nickel, and calcium were prepared by precipitating these oleates from a solution of sodium oleate. These soaps were dissolved in benzene and were then used as protective colloids. These colloids give promise of good results. It was soon seen that the magnesium oleate was the most satisfactory and consequently nothing more than preliminary experiments were made with the others. Starting with a mixture containing 20 percent water and 5 cc of a concentrated solution of magnesium oleate in benzene, it was possible to prepare an emulsion of water in benzene. On adding water to this little by little, the water content could be run up to 80 percent before the emulsion cracked. The emulsions are homogeneous only between 75 per cent and 80 percent water. At lower concentrations two liquid layers were formed just as in the case of the sodium oleate emulsions of benzene in water. The homogeneous emulsions were moderately stable, standing up for several days without cracking.

It was next discovered that the addition of a small amount of sodium oleate solution made the emulsion of water in benzene much more stable. Within certain limits there was no tendency to form emulsions of benzene in water. The data in Table V show that the change to emulsions of benzene in water occurs only when 6 cc of 5 percent sodium oleate solution have been added. These 50 percent emulsions formed

TABLE V

Total volume, 40 cc; 5 cc conc. Mg oleate in benzene; 15 cc benzene; percentage water, 50; time of shaking, 10 minutes

Water	Sodium oleate	Type of emulsion
19 cc	1 cc (1 percent)	Water in benzene
18 cc	2 cc (1 percent)	Water in benzene
17 cc	3 cc (1 percent)	Water in benzene
19 cc	1 cc (5 percent)	Water in benzene
18 cc	2 cc (5 percent)	Water in benzene
16 cc	4 cc (5 percent)	Water in benzene
14 cc	6 cc (5 percent)	Benzene in water
10 cc	10 cc (5 percent)	Benzene in water

two liquid layers at once; but there was no apparent further change after standing five weeks.

A number of experiments were made to see how high the water content could be brought in a homogeneous emulsion. I started with 5 cc conc. magnesium oleate + 1 cc 5 percent sodium oleate + 4 cc water. This was shaken vigorously and water was added in 2 cc lots until 50 cc had been added. This gave a stiff, homogeneous emulsion, containing about 92 percent water by volume. This emulsion stood up for two weeks before it cracked. The same original mixture was taken and water added in 2 cc lots as before; but 1 cc 5 percent sodium oleate was added after each 10 cc water. The resulting 92 percent emulsion was the most stable one obtained with a high water content. At the end of two months, it was apparently unchanged. This run was repeated in a 250 cc flask instead of a 100 cc bottle and water was added until the emulsion cracked. A homogeneous emulsion was obtained containing 96 percent water. These emulsions with high water content are quite instable, as a rule, and conditions have to be kept just right if one wishes to prepare a satisfactory emulsion. On the other hand, there is a good deal more latitude about the homogeneous emulsions containing about 75 percent water. A very satisfactory one can be made starting with 5 cc conc. magnesium oleate + 5 cc benzene + 9 cc water + 1 cc 1 percent sodium oleate, and adding 20 cc water in 2 cc lots. This emulsion is practically as stiff as those of higher concentration. After standing for eight weeks, there was no apparent change in this emulsion.

To show the general applicability of the method, some runs were made on the emulsification of water in carbon bisulphide. To 5 cc 2 percent magnesium oleate in carbon bisulphide + 5 cc 1 percent sodium oleate in water there were added 25 cc 0.01 percent sodium oleate solution in 1 cc lots and then 25 cc 0.01 percent sodium oleate in 2 cc lots. This gave a homogeneous emulsion of water in carbon bisulphide, containing 92 percent water by volume. In another run I started with 5 cc 2 percent magnesium oleate in benzene +

5 cc 1 percent sodium oleate in water to which were added 24 cc water in 1 cc lots and 46 cc water in 2 cc lots, while 1 cc 1 percent sodium oleate was added after each 10 cc water. The resulting emulsion contained 94.3 percent water and stood up for three days before cracking.

Increasing the relative concentration of sodium oleate must eventually change the type of the emulsion from water in carbon bisulphide to carbon bisulphide in water. This point was tested with a 50 per cent water emulsion which forms two layers, Table VI. The change comes when the ratio of sodium oleate to magnesium oleate rises about to unity.

TABLE VI

Total volume, 40 cc; 5 cc 2 percent magnesium oleate in CS_2; 15 cc carbon bisulphide; percentage water, 50; time of shaking, 10 minutes

Water	Sodium oleate	Type of emulsion
19 cc	2 cc (1 percent)	Water in carbon bisulphide
18 cc	2 cc (1 percent)	Water in carbon bisulphide
17 cc	3 cc (1 percent)	Water in carbon bisulphide
16 cc	4 cc (1 percent)	Water in carbon bisulphide
15 cc	5 cc (1 percent)	Water in carbon bisulphide
14 cc	6 cc (1 percent)	Water in carbon bisulphide
10 cc	10 cc (1 percent)	Carbon bisulphide in water
5 cc	15 cc (1 percent)	Carbon bisulphide in water

Some experiments with carbon bisulphide and water were also made with nickel oleate, calcium oleate, barium oleate, paraffin, spermacetin and guncotton as emulsifying agents. Though it was possible to prepare emulsions of water in carbon bisulphide, none of them were stable. Egg albumin was dissolved in a solution of caustic soda and precipitated by means of salts of zinc, aluminum, copper, magnesium, and calcium. The several precipitates were filtered and dried; but were found to be insoluble in carbon bisulphide and hence useless as emulsifiers.

A few experiments were made on paints to determine the nature of the emulsion. A mixed white paint; labeled "Eastlake Household Paint" was bought at a local store and also a sample of "white lead," labelled "Genuine White Lead" and made by the Empire Works. Raw linseed oil was obtained from the University paint shop. The drop test showed that oil was the external phase in the mixed paint. To 22 cc mixed paint in a bottle there were added 70 cc water in 5 cc lots, the bottle being shaken after each addition of water. A homogeneous emulsion of water in oil was formed which did not differ materially in consistency from the original paint. This emulsion contained 71.5 percent water plus the undetermined amount of water in the original paint. Ten grams of the "white lead" were now mixed with 10 cc linseed oil and 70 cc water added in 10 cc lots. An emulsion of 87.5 percent water in 12.5 percent oil was formed; but it cracked at the end of two days. These experiments were conclusive as to the formation of an emulsion of water in oil; but they left the question of emulsifying agent open. A qualitative test of the "white lead" showed the presence of lead, zinc, barium, and calcium; and of carbonates, sulphates, and silicates or silica. About 5 grams of each of the substances, zinc oxide, basic lead carbonate, lime, calcium carbonate, barium sulphate, lead sulphate, and silica were shaken up with 25 cc raw linseed oil and 25 cc water. Homogeneous emulsions were obtained in all cases; they seemed to be most stable with zinc oxide and least stable with silica. The differences were not great, however, and the experiments did not seem to bring out anything that was not known before. Since it was not at all clear why these substances should behave so much alike, or why they should give water in oil emulsions, it seemed well to try oil and water alone. A thick homogeneous emulsion of water in oil was obtained by shaking together 20 cc raw linseed oil and 20 cc water. This emulsion stood up indefinitely. On testing the linseed oil for rosin with the "Liebermann-Storch" test and the sulphuric acid color test, positive results were obtained by each method. The rosin is undoubtedly the emulsifying agent, both with the oil and in the case of mixed paints. Though Pickering[1]

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[1] Jour. Chem. Soc., 91, 2008 (1907).

has shown that emulsions can be made with insoluble emulsifiers, his experiments showed that the substances he used gave rise to emulsions of kerosene in water and not to emulsion of water in kerosene. Since rosin would naturally give rise to an emulsion of water in oil, the assumption of rosin as the emulsifying agent clears up the theoretical difficulties.

The general results of this paper are as follows:

(1) A satisfactory general method has been devised for determining which phase is the external one in an emulsion.

(2) When benzene and water are emulsified by means of sodium oleate, the water is always the external phase.

(3) It was possible to obtain homogeneous emulsions containing up to 0.5 per cent benzene by volume, and from about 80 percent up to 99 percent benzene. Intermediate emulsions separated into a creamy upper layer and a watery lower layer.

(4) The failure to obtain a continuous series of homogeneous emulsions of continuously varying properties is due to the experimental difficulty in making the drops of benzene so small that the Brownian movements will keep the drops distributed uniformly through the water. The larger drops rise and pack together.

(5) With my shaking machine, homogeneous emulsions with high concentrations of the liquid forming the internal phase, could be obtained only by adding that liquid gradually.

(6) It is possible to make a stiff jelly out of 99 cc benzene, 1 cc water, and about 0.05 gram sodium oleate. This jelly did not change perceptibly in six weeks.

(7) It is possible to make a stiff jelly out of 99 cc benzene, 1 cc water, and about 0.05 gram hard soap; but this jelly cracked inside of a week.

(8) It is possible to make a stiff jelly out of 98 cc benzene, 2 cc water, and about 0.02 gram sodium oleate. Cutting down the amount of sodium oleate to two-fifths, decreases the maximum volume percentage of benzene from 99 to 98.

(9) No emulsions of water in oil are formed when olive oil and water are shaken with soap, with sodium oleate, or

with caustic soda. What Robertson thought was an emulsion of water in oil was merely sodium oleate or the sodium salt of other fatty acids suspended in oil.

(10) It is possible to make a stiff emulsion out of 97 percent olive oil, 3 cc water, and about 0.15 gram sodium oleate.

(11) Magnesium oleate is the best emulsifying agent yet tried for making an emulsion of water in benzene. The emulsions are much more stable if a little sodium oleate is also present.

(12) Depending on the relative amounts of magnesium oleate and sodium oleate we get emulsions of water in benzene or of benzene in water.

(13) Using proper proportions of magnesium oleate and sodium oleate, it was possible to make an emulsion of water in benzene containing 96 percent water by volume.

(14) With my shaking machine, homogeneous emulsions of water in benzene could be obtained between the approximate limits of 75 percent and 96 percent water by volume. These limits have no theoretical significance and would be changed by more perfect emulsification.

(15) With perfect emulsification it is probable that there would be a marked increase in viscosity at or near the point where the internal phase constitutes 74 percent by volume of the emulsion because the globules would begin to be deformed by contact as the concentration increased above this value.

(16) Using proper proportions of magnesium oleate and sodium oleate, it was possible to make an emulsion of water in carbon bisulphide containing over 94 percent water by volume. This emulsion cracked at the end of three days.

(17) In mixed paints, water is the internal phase and oil the external one. By shaking a commercial white lead together with raw linseed oil and water, a water in oil emulsion was obtained containing 87.5 percent water and 12.5 percent oil by volume. This emulsion cracked at the end of two days.

(18) On shaking raw linseed oil and water together, an emulsion of oil in water was obtained. Rosin proved to be the

emulsifying agent and this is undoubtedly the usual emulsifying agent in the case of mixed paints.

(19) The pigments themselves cannot usually be the emulsifying agent in the case of mixed paints because Pickering's work on insoluble emulsifiers shows that most pigments would tend to produce emulsions of oil in water in so far as they had any emulsifying action.

(20) Whether one liquid is emulsified in a second or the second in the first depends on the nature of the emulsifier. A hydrophile colloid will tend to make water the external phase and a hydrophobe colloid will tend to make water the internal phase.

(21) In order to be a good emulsifying agent, a hydrophile or a hydrophobe colloid must be able to form a suitably coherent film round the internal phase. It is consequently not possible to obtain an emulsion starting with any colloid.

(22) There is no necessary connection between the initial stiffness of the emulsion and its permanency. In a permanent emulsion the film round the globules of the emulsified phase must not age much.

(23) When an emulsion of benzene, water, and sodium oleate was frozen, the emulsion cracked. When thawed and shaken, the mixture did not emulsify again. This is undoubtedly due to the fact that the sodium oleate did not redissolve readily in the water under the conditions of the experiment.

This work was suggested by Professor Bancroft and was carried out under the supervision of Mr. T. R. Briggs.

Cornell University
June, 1912

ACTION OF PERSULPHATES ON ACETATES

BY M. A. GORDON

When a solution containing sodium persulphate and acetic acid or sodium acetate is heated, a mixture of gases is given off, consisting of carbon dioxide and one or more hydrocarbons. The amount of carbon dioxide and the nature of the hydrocarbon may be varied by changing the conditions. One of the reactions seems to be a catalytic decomposition of acetic acid into methane and carbon dioxide,

$$CH_3CO_2H = CH_4 + CO_2.$$

It did not seem possible that persulphate itself could be the catalytic agent; but a process of elimination leads to this conclusion. The most plausible hypothesis was that platinum in some form, was the catalytic agent and consequently pieces of smooth platinum and of platinized platinum were immersed in the solution without any effect. In order to remove any hypothetical noble metal, including platinum, lead strips were placed in the persulphate solution so as to precipitate any unknown metal more noble than lead. This also had no effect. The addition of iron salts or of manganous salts do not increase the yield of methane. In order to show that the real catalytic agent was the persulphate itself, a solution of persulphate was heated long enough to destroy all the persulphate and was then added to the acetate solution. No decomposition into methane took place though the impurities in the persulphate were presumably still present. This last experiment seems to furnish conclusive proof that persulphate or an intermediate decomposition product of it is the catalytic agent. We may reject the hypothesis of an intermediate decomposition product being the catalytic agent because there is no relation between the amount of persulphate decomposed and the yield of methane.

Since other reaction products are usually formed besides methane and carbon dioxide, other reactions also take place. We may have complete or partial oxidation of the acetic acid by the persulphate, the reaction products being water and carbon dioxide, ethylene, or ethane. It is not yet known whether glycollic acid, methyl alcohol and other oxidation products are formed under any conditions.

The usual form of apparatus for the evolution of the gas consisted of a bottle (the volume of which was slightly greater than that of the solution) immersed in a water bath. The bottle was fitted with a rubber stopper and a capillary tube leading to a sample gas pipette filled with mercury.

The acetate solution (about half the total volume) was placed in the bottle and brought to the temperature of the bath. The persulphate was heated to about 60° C (at a higher temperature the solution gave off gas) and then added to the acetate. About 100 cc (unless otherwise stated) of the gas were collected for analysis. The pressure was kept fairly constant during the run.

The Dennis modification of the Orsat apparatus[1] was used for the analysis of the gas. Friedrichs' spiral pipettes[1] were used for the absorbing liquid. Mercury was used as the confining liquid in a water-jacketted burette. The surface of the mercury was kept wet with a few drops of water in order that the gas might be saturated with aqueous vapor at all times. The burette was washed out after using such liquids as fuming sulphuric acid, cuprous chloride, etc.

Considerable difficulty was experienced in obtaining satisfactory results for the unsaturated hydrocarbons soluble in fuming sulphuric acid. A Friedrichs' spiral pipette, containing 25 percent sulphuric acid, was used. The absorption was quite rapid at first, but slowed up after a few passages through the reagent. Table A shows this:

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[1] Dennis: Jour. Ind. Eng. Chem., 4, 898 (1912).

TABLE A

The data for this table were obtained during the analysis of the gas given in Table VI

Time passed through fuming H_2SO_4	Volume[1] cc I	Volume[1] cc II
0	9.9	10.2
1	44.9	44.8
2	47.5	47.4
3	48.0	48.0
4	48.2	48.1
5	48.5	48.4

Methane and ethane were slowly absorbed by fuming H_2SO_4.[2] It may be that, with the more efficient absorption due to the Friedrichs spiral pipette, some of the saturated hydrocarbons are taken out.

Hydrogen was tested for by means of palladium black, but the results were not satisfactory, as there was an increase in volume, due to CO_2 being given off. The copper oxide method[3] was then tried. The gas was passed through a tube containing copper oxide heated from 250°–260° C. The copper oxide was prepared by heating the commercial copper oxide in a hard glass ignition tube, in a current of air freed from CO_2.

Carbon dioxide was given off as in the case of the palladium black. Apparently, this was due to CO_2, which had been occluded by the copper oxide and not due to the burning of the hydrocarbon, for, on passing the gas through KOH, it was brought back to its original volume. No hydrogen was present.

Trouble was experienced in completely burning the gases in the combustion pipette. It was not discovered until a number of experiments had been made that the combustion was not complete even with an excess of oxygen. A second combustion was necessary, after passing the gas through KOH to remove the CO_2.

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[1] Gas not passed through KOH before volume is read.

[2] Worsatt: Jour. Am. Chem. Soc., 21, 245 (1899).

[3] Dennis: "Gas Analysis," 198 (1913).

Confirmation of this is found in some work by Hempel.[1]

"Numerous experiments with the Winkler-Dennis combustion pipette, show that it is extremely difficult to completely burn mixtures of methane and nitrogen, as part of the methane easily escapes combustion. Where one employs a combustion pipette filled with mercury and heats the mixture of oxygen, nitrogen and methane with the platinum spiral for a long time, in order to obtain complete combustion, the surface of the mercury becomes covered with a film of mercuric oxide. One naturally obtains a too high contraction due to the formation of this oxide of mercury."

Under "contraction ratio" in the tables is given the ratio of the volume contraction on combustion to the volume of the carbon dioxide formed. This ratio is 2.00 in the case of methane and 1.25 for ethane.

Under some conditions the hydrocarbon gas is pretty nearly pure methane. In Table I incomplete combustion probably accounts for the contraction ratio being 2.03 instead of 2.00. No free hydrogen is formed:

TABLE I

Sodium persulphate (70 percent)	6.3 grams
Sodium acetate (cryst.)	23 grams
Acetic acid (glacial)	100 cc
Water	100 cc
Temperature	75°–80°

About 500 cc of gas collected after passing through KOH solution.

Analysis of gas (freed from CO_2)

Olefines cc	Combustion			Volume hydrocarbon cc	Contraction ratio
	O_2 added cc	Contraction cc	CO_2 cc		
1.4	72.7	71.5	35.2	34.8	2.03
1.6	77.4	76.4	37.6	37.4	2.03

The favorable conditions for the formation of methane seem to be a relatively low concentration of sodium persulphate

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[1] Hempel: Zeit. anorg. Chem., 25, 1841 (1912).

and a high concentration of sodium acetate and acetic acid. A dilute solution of persulphate is more stable than a concentrated one and consequently there is less decomposition in the unit time and less oxidation of the acetic acid. It seems not unreasonable that a high concentration of acetic acid should be favorable to the methane dissociation. The part played by the sodium acetate is not entirely clear. It is, of course, a simple matter to say that undissociated acetic acid is the active mass and that sodium acetate forces back the dissociation; but acetic acid is dissociated so slightly that one would hardly expect the change in the degree of dissociation to be very important. It is also possible that the dissociation of sodium persulphate is forced back by another sodium salt. This would account for the beneficial effect of sodium sulphate.

The data in Table II illustrate the effect of varying the amount of sodium acetate, the concentration ratio increasing from 1.94 to 2.00.

TABLE II

Sodium persulphate (56.7 percent)	1.68 grams
Sodium acetate (cryst.)	*x* gram
Acetic acid (glacial)	20 cc
Water	20 cc
Temperature	98°–99°

Analysis of hydrocarbon gas

Sodium acetate g	Combustion			Volume hydrocarbon cc	Concentration ratio
	O_2 added cc	Contraction cc	CO_2 cc		
0.00	41.1	39.9	20.2	19.0	1.94
0.66	68.9	68.4	34.2	33.7	1.98
0.66	70.8	69.8	34.7	33.7	1.99
2.3	78.0	78.9	38.2	37.8	2.01
2.3	68.9	66:6	33.3	31.8	2.00

The data in Table III show the effect of varying the concentration of another sodium salt, sodium sulphate. With increasing concentration of sodium sulphate, the concentration ratio increases from about 1.70 to 1.90. The lower concentration of acetic acid causes a drop in the concentration ratio from 1.94 (Table II) to 1.72 (Table III).

TABLE III

Sodium persulphate (70 percent)	1.28 grams
Sodium sulphate (anhydrous)	*x* gram
Acetic acid (glacial)	1 cc
Water	20 cc
Temperature	98°-99°

Analysis of hydrocarbon gas

Sodium sulphate g	Combustion			Volume hydrocarbon cc	Concentration ratio
	O_2 added cc	Contraction cc	CO_2 cc		
0.0	31.7	30.2	17.4	16.3	1.74
0.0	36.5	33.7	20.0	17.7	1.69
2.0	41.9	39.9	21.1	19.5	1.90

In Table IV are given special data to illustrate the effect of changing the concentration of acetic acid. One cubic

TABLE IV

Sodium persulphate (56.7 percent)	1.68 grams
Volume of solution	40 cc
Temperature	98°-99°

No.	Acetic acid cc	Sodium acetate g	Water cc
1	20	2.3	20
2	20	2.3	20
3	1	—	39
4	1	—	39
5	—	2.3	40
6	—	2.3	40

No.	Combustion			Volume hydrocarbon cc	Concentration ratio
	O_2 added cc	Contraction cc	CO_2 cc		
1	78.0	76.9	38.2	37.8	2.01
2	68.9	66.6	33.3	31.8	2.00
3	37.3	35.3	18.3	16.9	1.93
4	31.4	30.0	15.5	14.3	1.93
5	50.1	43.4	25.6	19.7	1.69
6	56.0	46.9	27.9	19.6	1.68

centimeter glacial acetic acid is equivalent to 2.3 grams $CH_3CO_2Na.3H_2O$.

In the following experiments, Table V, the concentration of sodium persulphate was kept relatively high, with a corresponding decrease in the concentration ratio, which drops to 1.45. The gas contained considerable quantities of olefines soluble in fuming sulphuric acid:

TABLE V

Sodium persulphate (70 percent)	1.92 grams
Sodium acetate (cryst.)	0.14 gram
Acetic acid (glacial)	0.1 cc
Water	20 cc
Temperature	98°-99°

Analysis of hydrocarbon gas

Combustion		CO_2 cc	Volume hydrocarbon cc	Contraction ratio
O_2 added cc	Contraction cc			
23.8	19.7	13.2	10.5	1.49
23.7	19.7	13.6	10.0	1.45
29.1	23.8	16.4	11.5	1.45
28.7	24.8	16.3	13.2	1.52

Another run was made at a lower temperature, Table VI, in which the olefines were removed by means of fuming sulphuric acid before the hydrocarbon gas was analyzed:

TABLE VI

Sodium persulphate (70 percent)	96 grams
Sodium acetate (cryst.)	7 grams
Acetic acid (glacial)	5 cc
Water	1000 cc
Temperature	75-78°

About 500 cc gas collected after passing through KOH solution.

Analysis of hydrocarbon gas (freed from olefines)

Olefines cc	Combustion		CO_2 cc	Volume hydro-carbon cc	Contraction ratio
	O_2 added cc	Contraction cc			
38.8	32.8	30.7	16.6	15.0	1.85
38.4	33.0	30.7	16.8	14.8	1.85

The hydrocarbon gas left after the removal of the olefines appears to consist of a mixture of methane and ethane. Calculations based on the combustion, oxygen consumed, and volume of hydrocarbon, check quite closely with the theoretical. The hydrocarbon gas, therefore, consists approximately of 72 percent olefines, 22.4 percent methane, and 5.6 percent ethane. The composition of the olefines has not been determined satisfactorily as yet, but we are evidently dealing with a mixture.

In Tables I-VI the important point has been the composition of the hydrocarbons and no data have been given for the carbon dioxide set free during the reaction. If no acetic acid is oxidized completely to carbon dioxide and water and if there is no lower, non-gaseous, carbon compound formed, such as methyl alcohol for instance, the amount of carbon dioxide set free during the reaction should be equal to that produced by combustion of the hydrocarbon gases. A ratio greater than unity indicates some oxidation of acetic acid to carbon dioxide and water. Conditions which favor the decomposition of the persulphate, such as acidity, rise of temperature, etc., should increase the oxidation as shown by the CO_2 ratio or the ratio of CO_2 produced during the reaction to the CO_2 produced by the combustion of the saturated hydrocarbons. In Table VII are given data for the effect of temperature under condition such that the hydrocarbon is practically pure methane, the contraction ratio being approximately 2.00:

TABLE VII

Sodium persulphate (56.7 percent)	1.68 grams
Sodium acetate (cryst.)	4.6 grams
Acetic acid (glacial)	20 cc
Water	20 cc

Temp.	Reaction CO_2 cc	Combustion CO_2 cc	Contraction ratio	CO_2 ratio
98°-99°	41.1	34.5	2.02	1.19
98°-99°	22.0	18.4	2.01	1.20
98°-99°	34.1	34.8	1.99	1.24
78°-79°	33.8	31.1	2.00	1.09
78°-79°	33.0	31.4	1.97	1.05
64°-65°	31.9	30.0	1.99	1.06

Even at the highest temperature, the amount of acetic acid oxidized is only one-fifth that decomposed catalytically, and the value drops nearly to one-twentieth at the lower temperatures:

In Table VIII are similar data for cases in which relatively large amounts of ethane and unsaturated hydrocarbons are formed, the contraction ratio being distinctly less than two:

TABLE VIII

Sodium persulphate (70 percent)	1.92 grams
Sodium acetate (cryst.)	0.14 gram
Acetic acid (glacial)	0.1 cc
Water	20 cc

Temp.	Reaction CO_2 cc	Combustion CO_2 cc	Contraction ratio	CO_2 ratio
98°–99°	42.1	16.2	1.45	2.55
98°–99°	43.3	16.3	1.52	2.66
78°–79°	64.5	33.8	1.51	1.91

Tables VII and VIII indicate that temperature has little or no effect on the composition of the hydrocarbon as the contraction ratio does not change with change of temperature.

Even at the lower temperature nearly twice as much acetic acid is burned to carbonic dioxide and water as is converted into methane and ethane. If the solution is made distinctly acid with sulphuric acid, the decomposition of the persulphate takes place so rapidly that large amounts of oxygen are set free. This is shown in Table IX, the persulphate concentration being extremely high:

TABLE IX

Sodium persulphate (70 percent)	1.28 grams
Acetic acid (glacial)	1 cc
H_2SO_4 (sp. gr. 1.84)	5 cc
Water	9 cc
Temperature	98°–99°

Reaction CO_2 cc	Combustion CO_2 cc	CO_2 ratio	O_2 set free cc
5.2	0.8	4.5	42.0

If the persulphate concentration be kept down and if sodium sulphate be added, a small amount of sulphuric acid can be added without causing evolution of oxygen. The oxidation ratio is high under these circumstances.

TABLE X

Sodium persulphate (56.7 percent)	1.68 grams
Acetic acid (glacial)	1 cc
Sodium sulphate (hydrated)	3.2 grams
Sulphuric acid (sp. gr. 1.84)	1.0 gram
Water	39 cc
Temperature	98°–99°

Reaction CO_2 cc	Combustion CO_2 cc	Contraction ratio	CO_2 ratio
46.1	10.3	1.94	4.48
45.4	10.6	1.90	4.28

Addition of 1 cc molar manganous sulphate to a solution containing 1.68 grams sodium persulphate (56.7 percent), 1 cc glacial acetic acid and 39 cc water caused an increase in the carbon dioxide ratio to 7.05, a manganese oxide precipitating. A piece of platinum foil with a surface of 200 cm^2 also acted as a catalytic agent increasing the carbon dioxide ratio from about 3.0 to about 4.0.

It seemed desirable to determine, if possible, the relation between persulphate decomposed and carbon dioxide set free during the reaction. Preliminary experiments indicated that persulphate could be determined in presence of acetate by adding an excess of ferrous sulphate to the solution acidified with sulphuric acid. The analysis for persulphate was made by adding, to the mixed persulphate and acetate solution, 100 cc of ferrous ammonium sulphate solution (30 grams per liter), 10 cc H_2SO_4 (1 : 4), and 100 cc boiling water. The solution was then heated to 50°–70° C and titrated rapidly with $N/5$ $KMnO_4$. The results have been calculated on the assumption that part of the CO_2 comes from the catalytic decomposition of the acetic acid. Only the excess of CO_2 over that equivalent to the methane is considered as due to oxidation by persulphate. On this basis only half the active oxygen of the persulphate seems to be accounted for and there must be some other product which has not yet been isolated. It is possible that this may be glycollic acid since Professor Orndorff tells me that he has obtained glycollic acid by slow oxidation of acetic acid with permanganate. This would be the first oxidation product in case the oxidation takes place in stages, as it probably does. The data are given in Table XI:

TABLE XI

Sodium persulphate (56.7 percent)	0.84 gram
Sodium acetate (cryst.)	2.3 grams
Acetic acid	10 cc
Water	10 cc
Temperature	98°–99°

Analysis of hydrocarbon gas

No.	Combustion			Volume hydrocarbon cc	Contraction ratio
	O_2 added cc	Contraction cc	CO_2 cc		
1	38.2	36.9	18.4	17.6	2.01
2	69.8	68.1	34.3	33.2	1.99
3	71.0	69.1	34.8	33.6	1.99

No.	CO_2 cc	CO_2 ratio	O_2 lost $Na_2S_2O_8$ Grams	O_2 found CO_2 Grams
1	22.0	1.20	0.0135	0.0056
2	42.0	1.23	0.0225	0.0111
3	43.1	1.24	0.0239	0.0119

The general results of this paper are:

(1) Persulphates decompose acetic acid catalytically into methane and carbon dioxide.

(2) Persulphates oxidize acetic acid, some of the products being ethane, olefines, carbon dioxide and water.

(3) The catalytic decomposition is favored by high concentration of acetic acid, low acidity, and low concentration of persulphate.

(4) Low acidity together with high concentration of acetic acid can be obtained by adding sodium acetate to force back the dissociation.

(5) Conditions favoring the decomposition of persulphate increase the oxidation of acetic acid if not carried to an excess.

(6) High concentration of persulphate, high temperature, moderate acidity, presence of manganous sulphate or platinum foil, increase the oxidation of acetic acid.

(7) Addition of too much sulphuric acid makes persulphuric acid so instable at high temperatures that oxygen is set free and the oxidation of acetic acid is cut down correspondingly.

(8) Temperature has no effect on the composition of the hydrocarbon gas.

(9) Impurities in the persulphate are apparently not the catalytic agents because no probable impurity acts in this way and because the catalytic action ceases when the persulphate is destroyed.

This research was suggested by Professor Bancroft and has been carried on under his supervision.

Cornell University

OSMOTIC PRESSURE AND MOIST AIR

BY WILDER D. BANCROFT

Barring effects due to gravity, one should get the same osmotic pressure by placing the cell with the semipermeable membrane in saturated water vapor as though one immersed it in water as is usually done. Last year I came across an instance of this in the literature[1] which seems interesting enough to reproduce.

"In September, 1851, attention was attracted to an unusual increase of weight in a shipment of molasses, which occurred in the London Docks; it was some time before the cause could be discovered, and the steps taken to ascertain it ended in the perfect assurance that it was due to absorption. The great extent to which the action had taken place, and the large amount of property in our dock warehouses, which is thus proved to be occasionally affected by it, lead me to believe that a detailed account of this extraordinary instance may prove acceptable to the Society. For the following particulars I am indebted to the Mr. Muggeridge, of the London Docks, in whose care the molasses were stored, and by whom the progress of the action was watched:

"In August, 1849, a quantity of molasses were housed for the first time in a damp cellar, where they lay until September, 1851, when the increase of weight was observed. In order to ascertain its amount, the whole of the casks of the importation were re-weighed, when it was found that every cask which had not lost a portion of its contents by breakage, had gained considerably in weight. The casks were coopered and made tight, and in February, 1852, were again weighed, when (where breakage had not occurred) a further increase was found to have taken place. The total weight of the shipment was 1270 cwt. It was stored in 110 casks, containing from 11 to 12 cwt each. The increase on different casks

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[1] Ferguson: Jour. Chem. Soc., 6, 122 (1854).

varied considerably, reaching in some cases 38 lbs or about 3 percent of the contents. The total observed increase was 23¼ cwt or about 1.83 percent. This does not represent the total real increase, for it would appear that in some casks the absorbed water had just been sufficient to cover the loss from breakage, but not tell as increase; and there does not seem to have been one cask which had not suffered more or less loss. The real increase of weight due to absorption must have been much greater than that shown by the weighings. Important as this result was to the merchant, it was greatly exceeded by one that was afterwards observed, and which was as follows: A quantity of molasses imported in large tanks, were, in July, 1849, racked into 347 puncheons, weighing about 12 cwt each, the total weight being 4160 cwt; they were stowed in a lofty cellar, where they remained till September, 1852, when they were re-weighed for delivery. At various times some of the casks were found with heads bulging out from internal pressure, although none of them were full when housed, and it was necessary to draw off a portion to prevent them from bursting. When the bung started, the molasses rushed out with great force, ascending several feet to the roof of the cellar. On re-weighing, the increase was, as before, found to be different in different casks. On 52 there was a loss from breakage, 248 had gained from 1 lb to 30 lbs each, 67 from 30 lbs to 40 lbs, and 20 from 40 lbs to 51 lbs each. The total increase of weight on the shipment was 56 cwt. If we take the casks on which this increase took place, laying aside the 52 on which there was loss, the excess of absorbed water over the leakage was about 1.6 percent; in some of the casks it had reached as high a percentage as 4.25. A third case was also observed in December, 1848. 500 puncheons were filled from tanks in which they had been imported, and stored in the same cellar till July, 1852, when some of them were re-weighed with the same various results as to increase: 5 puncheons gave the following results:[1]

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[1] [Weights presumably cwt, st, lbs. W. D. B.]

No. 1, weight	11	3	13 lbs	gained 23 lbs.
No. 2, weight	11	1	7 lbs	gained 31 lbs.
No. 3, weight	12	0	7 lbs	gained 40 lbs.
No. 4, weight	11	2	0 lbs	gained 45 lbs.
No. 5, weight	12	0	0 lbs	gained 68 lbs.

"This was the largest increase of weight, though on a large number of casks it reached nearly to the same percentage. In No. 5 the excess of water absorbed over any leakage that may have occurred is 5 percent. The bungs were at this time started, and the casks, which had been stored not quite full, were found full to overflowing. One cask which had lost 14 lbs, and another 9 lbs, were also full. We know that these casks had not been overdrawn. Now, to effect a loss of 14 lbs, 4 gallons of treacle must have been replaced by water, not taking into account the quantity which was required to fill the cask completely. In the case of No. 5, where the increases of weight was 68 lbs, the quantity of water absorbed must have been very great, for after supplying the loss due to leakage, (and all casks leak more or less), 6.8 gallons of water entered through the pores of the wood during a period of 3 1/2 years. These puncheons, in which this maximum effect took place, had been American meal-casks, made of Quebec timber, which is much more porous than the wood of which West India puncheons are usually made. The specific gravity of the freshly imported molasses of the last lot was 1.394, and when taken in July, 1852, was 1.375."

Of course we do not know that the wood was actually impermeable to the sugar though permeable to water, but at least a condensation and absorption of water vapor occurred, which exceeded in amount the outward flow or leakage, and which gave rise to such a pressure that many of the casks burst. This seems an admirable practical illustration of a theoretical case which is not usually discussed in text-books of physical chemistry.

Cornell University

THE APPROXIMATE MELTING POINTS OF SOME COMMERCIAL COPPER ALLOYS[1]

BY A. B. NORTON AND H. W. GILLETT

Introduction

In the course of investigations on brass melting furnaces it became necessary to know, to a point of commercial exactness, the melting points of a few of the common brasses and bronzes. The binary systems copper–tin and copper–zinc have been thoroughly worked out not only as to melting points, but as to the full phase rule relationships, and also in regard to tensile strength. The U. S. Alloy Research Board, under Thurston, studied the mechanical properties of the ternary system copper–zinc–tin in detail, but as pyrometers were not perfected at the time of this investigation, their temperature measurements were confined to very crude ones on the pouring temperatures of the two binary systems copper–tin and copper–zinc, made by pouring the molten alloy into water, measuring the rise in temperature of the water and figuring the pouring temperature from the assumed specific heat of the alloy. The method, though the only one available at the time, was so crude and subject to so many errors that the figures are of little or no value.

Work on the copper–zinc–tin system from the phase rule point of view is in progress at Cornell University, but no melting-point determinations have yet been made.

Thus, while the melting points of two binary systems are well known, those of the commercial casting alloys containing copper, zinc, tin and lead, or copper with two of the other components have had little or no study.

Lack of Data in the Literature on Ternary and Quaternary Melting Points

Very few figures on these can be found in the literature.

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[1] Published by permission of the Director of the Bureau of Mines. This paper is also published by the Bureau of Mines as Technical Paper 60.

Primrose[1] mentions pouring gun-metal (88 copper, 10 tin, 2 zinc) at 950° C (1740° F)[2] this temperature being far too cold and giving a very poor casting and one of very low tensile strength, hence evidently not far above the melting point.

This figure is probably not correct as 90 copper, 10 tin has a melting point of about 1005° C (1840° F) and 2 percent of zinc would probably not lower the melting point to such a degree.

Primrose[3] in a later paper shows a cooling curve for gun-metal 88 copper, 10 tin, 2 zinc containing less than 0.2 percent of lead, (exact analysis not given) which shows the melting point (liquidus) at 1010° C, or slightly above that for a corresponding zinc-free bronze, although some lowering of the melting point by the zinc might be expected.

Longmuir[4] also poured some alloys at a temperature at which the metal would just flow, and so cold that the castings were poor and the tensile strength very low. His alloys and temperatures are:

Gun-metal	965° C	1770° F
Yellow brass	850° C	1560° F
Red brass	1058° C	1935° F
Muntz metal	943° C	1730° F

These figures also are probably not accurate. The remark made on the earlier Primrose figure for gun-metal applies here. The composition of the alloys was not given. If it be assumed that the names given have their normal significance, yellow brass would be about 65 copper; 35 zinc, which melts at about 915° C (1680° F), and Muntz metal

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[1] Primrose, H. S.: "Metallography as an Aid to the Brass-founder," Metal Ind., 8, 466 (1910).

[2] Since the accuracy of temperature measurements at the melting points of the brasses and bronzes does not warrant figuring down to a degree, in transforming measurements taken in centigrade or in Fahrenheit to the other scale, the figures are rounded off to the nearest 5° or 10°.

[3] Primrose, H. S. and Primrose, J. S. G.: "Practical Heat Treatment of Admiralty Gun-metal," Jour. Inst. Metals (British), 9, 169 (1913).

[4] Longmuir, P., quoted by Law, E. F.: "Alloys and their Industrial Application," 1909, p. 10.

60 copper; 40 zinc, which melts about 890° C (1635° F). Muntz metal should certainly melt lower than yellow brass, not higher, as these figures give. Similarly, red brass, if of the common composition, (about 85 copper, 5 tin, 5 zinc, 5 lead) should melt below gun-metal, (taken as 88 copper, 10 tin, 2 zinc).

Karr[1] used a radiation pyrometer in determining the melting points and pouring temperatures of some copper alloys. For an alloy of 68.8 copper, 0.2 lead, 31 zinc, he got 1540° F (895° C), which he states is lower than the true melting point, evidently because of the well-known deviation from black body conditions of molten copper or its alloys. He gives 1650° F (900° C) as the melting point of one alloy containing 84 per cent copper; 1735° F (945° C) for that of another of the same copper content and 1850° F (1010° C) for another said to correspond to gun-metal but to contain no zinc. The exact composition of these alloys is not given.

Since the literature on the subject was found to be so meager it was decided to obtain figures on the melting points of a few typical commercial alloys with sufficient accuracy for the purpose in hand.

Methods Used in the Work

The alloys were melted in a gas furnace. Instead of using the ordinary shape of crucible which gives too large a surface for volatilization and oxidation, crucibles were made up from some bonded carborundum tubes which were in stock from a previous investigation.[2]

These were about 4.5 cm I. D. and had about 8 mm walls. They were cut to about 15 cm long and an artificial graphite plug fitted at one end to form the bottom, luting it into place by alundum cement. Considering the cost of machining out a crucible from a graphite rod as well as that

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[1] Karr, C. P.: "The Pouring and Melting Points of some High Grade Bronzes," Trans. Am. Brass Founders' Assn., 5, 78 (1911).

[2] For details of the carborundum tubes, see Gillett, H. W.: "Temperature Measurements in an Experimental Carborundum Furnace," Jour. Phys. Chem., 15, 225, 227 (1911).

of the graphite itself, these were much cheaper than artificial graphite crucibles, especially as they do not burn away anywhere near as fast as graphite. Their life was as good as that of the ordinary crucibles of fire clay plus graphite mixtures.

The temperatures were measured by a platinum, platinum-rhodium thermocouple used with a single-pivot galvanometer.

The couple has been calibrated against one which in turn has been checked against one calibrated by the Bureau of Standards, the secondary standard being read on a potentiometer, and the scale found to be correct within the limits of error of reading. The couple was also checked up by the melting points of copper, of common salt, and of a bronze 90 copper, 10 tin. The couple was correct within the error of reading, at these points.

As these calibrations were made with the cold junction at 20° C, the couple was used without icing the cold junction, the cold junction being so protected from the furnace that a thermometer at that point showed within 3° C of 20° C during all the runs.

The thermocouple wires were insulated by 1 mm bore 2 mm O. D. Marquardt Mass tubing, and the hot junction was slipped into a Marquardt Mass tube closed at one end, 30 cm long 5 mm I. D. 9 mm O. D. The open end of this was fastened into an open ended porcelain tube 35 cm long, 10 mm I. D. 14 mm O. D. by alundum cement. This arrangement served to protect the couple from zinc fumes or reducing gases.

The end of the Marquardt Mass protecting tube was in turn protected from the molten metal by an artificial graphite boot, 9 cm long and with 3 mm walls.

There is considerable time lag in the pyrometer reading when a cold protecting tube and boot is plunged into molten metal, but after the tube is once hot the lag is not great. As the melting points were not determined by noting when the metal solidified, but by plotting temperatures against time, the proper temperatures for the heat evolution on freezing or heat absorption on melting should be shown even if there was some lag.

About 600 grams of metal was used in making the tests, the metals were weighed out in the proper proportions to form the alloy desired, a slight excess of zinc, increasing with increasing zinc content, being allowed to compensate for volatilization. Electrolytic copper, Bertha zinc and chemically pure lead and tin were used. The copper was melted first, and covered with granular carbon and a little salt. When the copper was melted, the tin, the lead, and lastly the zinc was added, and the alloy well stirred with a graphite rod.

When the alloy was fully melted and mixed, the pyrometer was inserted and so clamped that the graphite boot did not touch the bottom or sides of the crucible. The gas flame was lowered and the temperature read every 15 seconds, stirring between each reading. When the alloy had frozen the gas was turned up and a heating curve taken. This was repeated several times. Zinc was continually volatilized in small amounts from the melts containing zinc, but not in sufficient amount to exert appreciable influence on the melting point, as duplicate runs agreed within 5° C in all cases. After the runs were completed, the melt was poured in most cases into an ingot mold, sampled and analyzed. As the analyses agreed well with the composition aimed at on the samples analyzed, the melts not containing zinc were not analyzed. Duplicate analyses of the same sample agreed within 0.1 percent.

All the melts were made up from virgin metals except the sample of manganese bronze which was in the form of test bar ends from a previous investigation.[1] It had given 76000 to 77000 lbs. per sq. in. tensile strength and 24 to 35 percent elongation in the standard brick form test bar. It was made up for

Copper	56
Zinc	41
Iron	1.5
Tin	0.9
Aluminum	0.45
Manganese	0.15

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[1] Gillett, H. W.: "The Influence of Pouring Temperature on Manganese Bronze," Trans. Am. Inst. Metals, 1912 (p. 207).

TABLE I

Alloy	Composition aimed at				Analysis				No. of duplicate determinations	Melting-Point Liquidus	
	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Cu		Deg. C	Deg. F
Gun-metal	88	2	10	—	—	—	—	—	4	995	1825
Leaded gun-metal	85.5	2	9.5	3	85.4	1.9	9.7	3.0	6	980	1795
Red brass	85	5	5	5	—	—	—	—	(2 samples) 8	970	1780
Low grade red brass	82	10	3	5	81.5	10.4	3.1	5.0	4	980	1795
Leaded bronze	80	—	10	10	—	—	—	—	3	945	1735
Bronze with zinc	85	5	10	—	84.6	5.0	10.4	—	4	980	1795
Half-yellow, half-red	75	20	2	3	75.0	20.0	2.0	3.0	3	920	1690
Cast yellow brass	67	31	—	2	66.9	30.8	—	2.3	4	895	1645
Naval brass	61.5	37	1.5	—	61.7	36.9	1.4	—	5	855	1570
Manganese bronze	—	—	—	—	—	—	—	—	6	870	1600
										all ± 10	all ± 20

As the figures were all reproducible to 5° C, an allowance of ± 10° C is probably ample to cover all errors of reading and of calibration and use of the pyrometer.

As it was first cast into ingot, then remelted and cast into test bars and these then remelted for melting-point determination, the zinc content was probably nearer 40 than 41 and the copper nearer 57 than 56 when the melting points were taken. This sample was not analyzed.

The melting point given is the liquidus, or point where freezing begins on cooling and ends on heating. This is more strongly marked than the solidus, or point where freezing ends on cooling or begins on heating.

Melting-Point Observations

The data are given in Table I on preceding page.

Binary Melting Points from the Literature

For comparison the melting-point (liquidus) figures for the binary systems copper-tin,[1] copper-zinc[2] and copper-lead[3] for the range covering the common industrial alloys are given below. These are scaled off from curves in the references given. As the curves are small the figures are only accurate to about ± 10° C or ±20° F.

TABLE II

Composition by weight		Copper-tin Melting point	
Copper	Tin	° C	° F
95	5	1050	1920
90	10	1005	1840
85	15	960	1760
80	20	890	1635

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[1] Shepherd, E. S. and Upton, G. B.: "Tensile Strength of Copper-tin Alloys," Jour. Phys. Chem., 9, 446 (1905).

[2] Shepherd, E. S.: "The Constitution of the Copper-zinc Alloys," Jour. Phys. Chem., 8, 423 (1904).

[3] Desch, C. H.: "Metallography (Copper-lead Alloys)," 1910, p. 85.

TABLE III

Composition by weight		Melting point	
Copper	Zinc	° C	° F
95	5	1070	1960
90	10	1055	1930
85	15	1025	1880
80	20	1000	1830
75	25	980	1795
70	30	940	1725
65	35	915	1660
60	40	890	1635

TABLE IV—COPPER–LEAD

Composition by weight		Melting point	
Copper	Lead	° C	° F
95	5	1065	1950
90	10	1050	1920
85	15	1035	1895

Acknowledgment

The melting points and analyses in Table I were obtained by Mr. A. B. Norton with aid from Mr. S. J. Popoff at Cornell University, under the direction of Prof. W. D. Bancroft of Cornell and of H. W. Gillett of the Bureau of Mines, in the alloy work in which the Department of Chemistry at Cornell is coöperating with the Bureau.

Cornell University

NEW BOOKS

Electric Furnaces in the Iron and Steel Industry. *By W. Rodenhauser and I. Schoenawa. Translated by C. M. von Baur. 23 × 16 cm; pp. iii + 419. New York: John Wiley & Sons, 1913. Price: $3.50.*—Previous to the appearance of this book, there was practically no single source of condensed information concerning the electric iron and steel industry. The book is, therefore, to be welcomed, since it places in compact form a lot of information which heretofore was scattered throughout the periodical literature. The English translation is important from the practical standpoint, since it is probable that a wide future is in store for the electric furnace in the United States. The book contains much practical as well as theoretical information.

After treating certain fundamentals, the requirements of an ideal furnace are considered. In the fundamentals such things as electrical units, power factor, heating, motor, and chemical effects, in the electric furnace, are considered. A general discussion of arc furnaces then follows, in which the electrodes are discussed at length. The method of treatment of the specific furnaces is to give the design, method of operation, etc., and then to compare this specific type with the ideal furnace. The authors realize that definite conclusions should not be drawn in regard to the best type of furnace, on account of the fact that specific conditions, different in different cases, may change the whole situation. In the discussion of electrodes of the arc furnace, a quotation, p. 94, from the book (will not be out of place), illustrating the care with which the authors draw conclusions.

"During the discussion of the electrode conditions, we have often compared the graphite with the carbon electrodes. Is therefore one recommended above the other? To this question this reply may be given: Graphite electrodes mainly have the advantage of greater resistivity, and greater mechanical firmness. This advantage, though, must be purchased at a far higher price, compared to carbon electrodes. Large electrode surfaces tend to save energy, and consequently it is better to work with low current densities."

"From all this it is apparent, that one would, at first, endeavor to utilize carbon electrodes, at least as long as these can still be made of good quality and at the desired cross-sections. It is only with the largest furnaces, where the cross-sections would become so large, that uncertainties would enter the operation, through breakages, for instance, that one would be willing to pocket the disadvantages of the graphite electrode, in order to gain the important advantage of definite and sure operating conditions."

A good discussion of the Stassano furnace and the Héroult furnace then follows. It is interesting to note the conclusion as to the practical limitation of the size of the Héroult furnace. From the quotation below it is evident that the best size in the case of the Héroult furnace is fifteen to twenty tons:

"Since then there has been built the furnace of 15 tons, as mentioned by Eichhoff. For this size the above deductions are correct, however, with the limitations that the furnace efficiency cannot be further increased by further increasing the size of the furnace unit. The efficiency of furnaces of increasing sizes with two electrodes follows the curve of a parabola. However, where three electrodes are used, the efficiency will naturally decrease, due to the higher thermal losses, which latter gradually reach the practical attainable minimum, with the increasing size of furnaces. As Héroult furnaces, however, are built today, these losses will not be less than 25 percent."

In comparison of the Girod with the Héroult furnaces, the following quotation may be given: "The opinion of Héroult that the series connection of the electrodes gives more useful work, is not substantiated in any way. We shall see later on, that the total electrode cross-section of the Héroult furnace is not greater than with the Girod furnace, disregarding entirely how incomprehensible it is that Girod does not also operate with the same current density and the same low current densities as Héroult does. It still remains to be proved that operation with low current densities is an advantage, irrespective of the size of the furnace . . . . Lastly we may add that, if we consider only the evenness of the current distribution, and the heat generation as above mentioned, these alone should be enough to decide the question. That there is an advantage in the lower voltage goes without saying. To these we might add the further advantages of the smaller current fluctuations, especially when melting down cold stock, while the opinion regarding the greater simplicity and the greater safety during the operation of one furnace over the other may be left to the reader."

General discussions of the induction furnaces, together with specific treatment of the Kjellin and Roechling-Rodenhauser furnaces, are then included. One of the advantages in favor of the induction furnace may be seen from the following:

"It has also been mentioned that the induction furnace undoubtedly has the best attainable *electrical efficiency* of any electric furnace, because all electrode losses are avoided, and hence only the transformer losses come into play with induction furnaces, except when a special generator is used, and then only the primary copper losses and iron losses appear in the transformer parts built into the furnace. Transformer losses are, however, present with nearly every arc furnace, thus a transformer is almost invariably erected as closely as possible to the furnace."

The electric shaft furnace is then treated in detail, in which the prevailing types of shaft furnaces are discussed. In review a number of proposed types of furnaces which have not been used commercially to any great extent, are then considered. The Keller furnace is treated here more as a Girod furnace with a modified bottom than otherwise. At the end of this part of the book a comprehensive table is given, where all the furnaces which have been built are listed. The names of the companies, the kinds of current used, sizes of the furnaces, kinds of charge, and the products formed, are given.

In the second part of the book, the first chapter treated, is on the materials used in furnace construction, then follows a chapter on electro-metallurgy of iron ores, a discussion of the reactions occurring in the electric furnace, and the use of the electric furnace in the preparation of special steels.

The book closes with this significant paragraph:

"The result of all this is that the electric furnace will not only play an important role in the future, but that it is already a factor which each iron and steel plant must now carefully consider."

The book is unquestionably the best of its kind which has been published in English. In the second part a large number of practical tests are included. The treatment, however, of theoretical and practical considerations separately, causes a lack of unity in the book which makes it more or less hard reading. The references to periodical literature are not numerous. The book is printed on excellent paper and contains a large number of excellent drawings.

C. W. Bennett

General Metallurgy. *By H. O. Hofman. 23 × 17 cm; pp. vii + 909. New York: McGraw-Hill Book Co., 1913. Price: $6.00.*—The preface states that the aim of the book is to cover the field of general metallurgy as a whole, that the point of view is that of the metallurgist who has a leaning toward physical chemistry, and that special attention has been paid to the mechanical apparatus used in metallurgy.

The book is long, but is concisely written, notwithstanding. Literally thousands of references add greatly to its value.

The proportioning of the subject matter in a book of this nature is a matter on which all readers cannot be suited. Even in a book of over 900 pages most readers will feel that the author has left the impression that Sam Weller said it was the great art of letter-writing to give—to make the reader wish there was more. The probable explanation of the omissions and condensations is that this volume is the first of a series, the rest of which will deal with the more specific problems of metallurgy. Yet it is a bit startling to find that Chapter V, ores, consists of one page. Some thirty pages are devoted to the phase rule applied to alloys, but the reader who can use these thirty pages will wish for more concrete applications of the theoretical diagrams for the different cases and will finally turn to Desch's "Metallography" instead. If this part of the book were to be included at all, one would wish the author had pointed out that equilibrium conditions in alloys are rare and that the equilibrium diagram is perhaps most useful as a basis for considering the deviations from it. When he comes to slags, the author gets down to business with the phase rule and makes a tool of it by many practical applications.

The discussion of the properties of metals gives what the metallurgist wants to know better than most books on materials of construction. The paragraphs on occlusion and diffusion of gases in metals, and on volatility of metals are particularly good.

On refractories, the book is almost up to the standard of Havard's "Refractories and Furnaces."

The book is in general, well up to date, many 1913 references being included. The discussion of electric furnaces is an exception to this, and is very sketchy.

One feels that the treatment of electrolytic refining is also a bit weak, but perhaps the author is saving a better discussion for later volumes of the series.

The classification of coals, peat and its briquetting, charcoal, coke, coal gas, producer gas, water gas, and the mechanism for their production are very well dealt with. There is considerable information on pulverized coal and on oil burners. The description of the mechanical appliances for ore crushing and concentration, for rolling, drawing and forging metal, of pumps, filter presses, chimney blowers, roasting blast and reverberatory furnaces, gas scrubbers, dust collection by the Cottrell and other processes, blast dryers, and of regenerators, are of immense practical value and are aided by many good illustrations.

Not content with helping the metallurgist out on his engineering problems, the author also gives him aid on the chemical side with a clear discussion of the reactions desired in roasting, smelting and fluxing, and in general with the fundamental chemistry of the metallic compounds dealt with in metallurgical work.

Colloids get brief mention in relation to clays and slimes.

There are few real errors, although on p. 59 we read "If two metals are to be alloyed, and one is volatile at the melting point of the other (*e. g.*, Zn and Cu) they are charged together in order that the readily fusible metal may dissolve the more refractory," which is not the case in making of yellow brass where the Cu is melted before "speltering."

On p. 377 the formation temperature of siloxicon is given about 1000° C too high, though that of carborundum, on the next page, is correctly given. Some errors in proof-reading show up—"violatile" p. 229, "7900° C," p. 247, "O" for o, p. 315, "CH_2" as a gas p. 22, "Rankine" for Rankin, p. 344, a 9 instead of a o in the figure in Table 144 for the heat conductivity of chromite brick, "alumdum" and "4450° C" p. 370, "Oratios" p. 437.

The discussion of pyrometers is quite long, but why include such things as expansion pyrometers and the thermophone and omit all mention of the Morse or Holborn-Kurlbaum instrument, or of base metal thermocouples? With the rather full description of the methods of manipulating bomb calorimeters and gas calorimeters, one would expect that one would be told enough of the operation of thermocouples to include more than a passing mention of cold junction corrections, and a little more practical information on protecting tubes. The limitations of the use of Seger cones, pp. 133, 438, are correctly stated.

The last chapter "Economic Considerations" is not of much actual value in itself, but one is glad to see even five pages on management, organization of work and cost accounts in a work of this sort, as it serves as a hint to the metallurgist that it is not out of place for one who may deal chiefly with fuels, ores, and furnaces, to know something about these other things.

The binding, paper, print, and illustrations are good.

The book is not only a general treatise, which will give the student a good idea of its field, but is also a reference book holding a vast amount of detailed information in its crisp sentences and its well chosen tables. It will be the book that the metallurgist will turn to first in search for information on almost any subject in his line. If he does not find the information itself, he is almost sure to find references that will give it. There are few chemists or engineers, even though working in fields far removed from the metallurgical, who would not find much of use to them in the description of mechanical processes.

It is the only book covering the broad field of general metallurgy, and it covers it well.
H. W. Gillett

Conférences sur quelques thèmes choisis de la Chimie physique. *By Svante Arrhenius. 14 × 23 cm; pp. 112. Paris: A. Hermann & Fils, 1912.*—This volume contains five lectures: the molecular theory; suspensions and the phenomena of adsorption; free energy; the atmospheres of the planets; physical conditions on the planet Mars. The first three were delivered at the Sorbonne, the fourth before the French physical chemical society, and the fifth before the French physical society.

In the second lecture Arrhenius introduces a new formula for the adsorption isotherm which he considers an improvement on Schmidt's. The improvement is not recognized as such by Schmidt. The last two lectures merely give, in condensed form, what has already appeared in other books that Arrhenius has written. As is well known, Arrhenius does not believe in the existence of canals on Mars. He considers that what we see are geotectonic fissures. Since Arrhenius also believes that +5° C is a high mid-day temperature on Mars in summer, of course he cannot see any object in irrigation even if there were canals.

Wilder D. Bancroft

Chemical German. *By Francis C. Phillips. 23 × 16 cm; pp. iii + 241. Easton: The Chemical Publishing Co., 1913. Price: $2.00.*—In the preface the author says:

"In the following pages an attempt has been made to provide students of chemistry with a course in German which will serve as an aid in reading the German literature of this science. Students of German, however proficient they may be in the classical literature of the language, find difficulties in mastering the German scientific nomenclature and such difficulties are increased by the lack of dictionaries giving correct meanings of scientific terms.

"Many textbooks on scientific German have appeared, but it has become common in the planning of such textbooks and in the teaching to regard scientific German as a subject that could be taught and studied rather remotely from the sciences concerned in the student's plan of work and, in attempting to cover the entire scope of the various sciences entering into university curricula, the fact has, to some extent, been overlooked that the German nomenclature of a single science should be studied by the student more systematically and in greater detail and after he has become sufficiently advanced in the science to grasp the meanings of technical terms and to understand their uses.

"Of the various sciences none is more indebted to the Germans for its past and present development than chemistry and the student of advanced chemistry is preëminently in need of a knowledge of German sufficient to enable him to read the best German chemical literature. There is need for a standardizing of the courses in scientific German. When this is secured it will probably be required that the student should have definite knowledge of the German nomenclature of the particular sciences in which he is partially specializing. For the attainment of a standard of knowledge there is need for textbooks upon the German of particular sciences.

"The present book is a contribution to the portion of scientific German which deals with chemistry. It contains rules of nomenclature interspersed with exercises intended to illustrate the use of German chemical terms pertaining to general chemistry, inorganic and organic, and to the various processes of the laboratory. These are followed by a collection of extracts from the writings of noted German chemists, having in many cases direct bearing upon the history of chemistry. A vocabulary of the more common German terms used in chemistry will aid the student in his translations. The work is intended for students who have had at least a year of German and who have mastered the elements of chemistry."

This seems like a good book and one that should be serviceable to the numberless students of chemistry, very few of whom now read German with any fluency. *Wilder D. Bancroft*

Liquid Steel, Its Manufacture and Cost. *By David Carnegie. 24 × 16 cm; pp. v + 520. New York: Longmans, Green & Co., 1913. Price: $7.50 net.*—In view of the rapid increase in the demand for steel in this and other countries, the author thinks that it is very important to educate men in the money value of different materials and processes used in steel manufacture.

"Several standard works on the metallurgy of steel, to which reference has been made in the following pages, deal, in some measure, with the cost of steel manufacture, but so far as I am aware no previous attempt has been made to compare systematically the costs of all the steel-making processes, having in view their metallurgical and engineering significance." This work has been undertaken therefore to meet this need. To the reviewer it is one of the most exhaustive books dealing with this phase of the subject. It represents a large amount of work, and is worthy of careful consideration. In the comparison of costs of similar processes, the following items are kept in mind throughout:

"1. All items of cost of manufacture are included up to that stage where the liquid steel is ready for use.

2. The steels produced in similar processes conform to the same standard of tests, unless otherwise stated.

3. The same outputs are taken during like periods.

4. The cost of raw materials, fuel, power, labor, etc., for like processes are taken at the same market value." One great value of the book depends on the care with which various cost items are given. All costs are carefully itemized, so that it is easy to change the author's estimate to meet local conditions.

This book is not only a comparison of the costs of liquid steel, but it is also a manual on liquid steel. The materials used in manufacture are carefully described; practically all the types of furnace are considered very carefully from the standpoint of American and European practice. For instance, in Chapter 2, a discussion of ores, pig iron, refractory materials, fluxes, fuels, and ferro-alloys is given; advantages and disadvantages of different types of materials, analyses and costs. The manufacture of special steel in the crucible furnace is then taken up in detail. Drawings of all important types of furnace, gas and coke fired; American and German furnaces, are given. Itemized costs of producing liquid steel are then included for the various types of furnace.

The history and development of the basic and acid Bessemer process are then considered in detail. Development of the converter with apparatus used in connection with it, and converter practice, in large and small plants are then given. Costs under different conditions are then included, both as to cost of machinery and cost of operation of plants.

The acid and basic open-hearth processes are described. The discussion of the development of the furnace is concluded with the following paragraph:

"From the foregoing descriptions it may be concluded that the modern open-hearth furnace differs only in small details from the original furnace designed by Siemens Brothers. The principle of regeneration is the same today as when applied in 1856 by Frederick Siemens. The introduction of the gas producer was a step forward, as the use of four instead of two regenerators became possible, hence both gas and air were heated before mixing in the furnace.

"The most noticeable feature of the modern furnace when compared with the first furnaces employed for steel making is the magnitude of the capacity. Furnaces of the fixed type are made as large as 180 tons' capacity, while the tilting furnace of the Talbot continuous type are made to take 250 tons." As before, the arrangement in large and small plants is discussed in more or less detail. Preparation of steel in the electric furnace next demands attention. After a discussion of the older furnaces, arc and induction type, there follows a short discussion of the later development in furnace practice.

The Frick, Hiorth, Paragon, Electro-metals, Nathusius furnaces are included. Short descriptions are given of the Cutts, Ruthenburg, Anderson, Chaplet, Levoz, Helberger, Hering, and Igewsky, furnaces which are probably of doubtful commercial value. Short descriptions of chemical reactions occurring in the electric furnace are given, with the costs of preparing liquid steel in the various furnaces.

At the end of these discussions are found tables where the costs of the different methods are assembled for comparison. A system of keeping and assembling works' costs, and a short chapter on the conditions of labor costs conclude the volume.

The book contains over a hundred tables, ten large plates, and over 250 cuts. It contains a large amount of data and information in a convenient form for ready reference. *C. W. Bennett*

Ubüngsbeispiele aus der unorganischen Experimentalchemie. *By Heinrich Biltz and Wilhelm Biltz. Second edition. 23 × 17 cm; pp. iii + 237. Leipzig: Wilhelm Engelmen, 1913. Price: 8 marks.*—The first edition was reviewed six years ago (12, 140). The present edition differs from the first "only in small though numerous changes." The seven experiments under the head of colloidal state are: Bredig's colloidal platinum; colloidal antimony sulphide; adsorption of iodine by charcoal; lanthanum blue; molybdenum blue; colloidal gold solutions; hydrogels as semipermeable membranes. *Wilder D. Bancroft*

Optique physique. *By R. W. Wood. Translated by H. Vigneron and H. Labrouste. Vol. I. 25 × 17 cm; pp. 424. Paris: Gauthier-Villars, 1913. Price: 16 francs.*—The second English edition of physical optics was reviewed (15, 707) two years and a half ago. There is to be a French edition in two volumes, of which the first volume has now appeared. The book was well worth translating and the translators are to be congratulated on making this work of Wood's available to French readers. *Wilder D. Bancroft*

SOME REACTIONS OF LIQUID ANHYDROUS AMMONIA AND ACETYLENE

BY F. G. COTTRELL

It has been shown by Moissan[1] that the blue solutions formed by sodium, potassium, lithium, and calcium in liquid ammonia are instantly decolorized when acetylene is run into them. Upon evaporation of the liquid the crystalline compounds $Na_2C_2.C_2H_2$; $K_2C_2.C_2H_2$; $Li_2C_2.C_2H_2.3NH_3$ and $CaC_2.C_2H_2.4NH_3$ are obtained. Upon gentle heating these lose ammonia and acetylene and the pure carbides remain. At higher temperatures all of these except calcium carbide decompose into their elements.

The following work had as its starting point the attempt to extend this method to the preparation of magnesium carbide which up to the present has apparently never been isolated in a pure state. The nearest approach to this, at the time this work was undertaken in 1906, being an experiment, also due to Moissan,[2] in which acetylene was passed over gently heated magnesium powder and a black mass obtained which in contact with water liberated acetylene and when heated in the electric furnace broke down into its elements. More recently Novák[3] by a quantitative physico-chemical study of the reaction of acetylene on metallic magnesium at temperatures from 500° C to 800° C, has definitely established the existence of the two carbides MgC_2 and Mg_2C_3, and indicated their relative ranges of stability with regard to temperature, but was unable to isolate either of them in a pure state.

While the preparation of a pure magnesium carbide was the original incentive for the present work, it soon became only an incident to the study of the wider range of reactions

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[1] Moissan: Comptes rendus, 127, 911 (1898).

[2] Ibid., 126, 302 (1898).

[3] Novák, J.: "Zur Kenntniss der Magnesiumcarbide," Zeit. phys. Chem., 73, 513-546 (1910).

here described. The non-formation of magnesium carbide in the electric furnace coupled with the determining influence which the content of magnesium in silicate fusions appears to exert upon the crystallization of carbon as diamond[1] both in nature and in the laboratory, make a knowledge of its properties, and especially its stability as regards temperature of considerable interest.

All of Moissan's work with liquid ammonia and acetylene was carried out in open vessels, *i. e.*, not far from the normal boiling point of the liquid ammonia (—33° C). At these temperatures magnesium is not appreciably attacked by mixtures of ammonia and acetylene. Higher temperatures and pressures were therefore imperative, and the following method was finally adopted as the result of a rather extensive series of experiments:

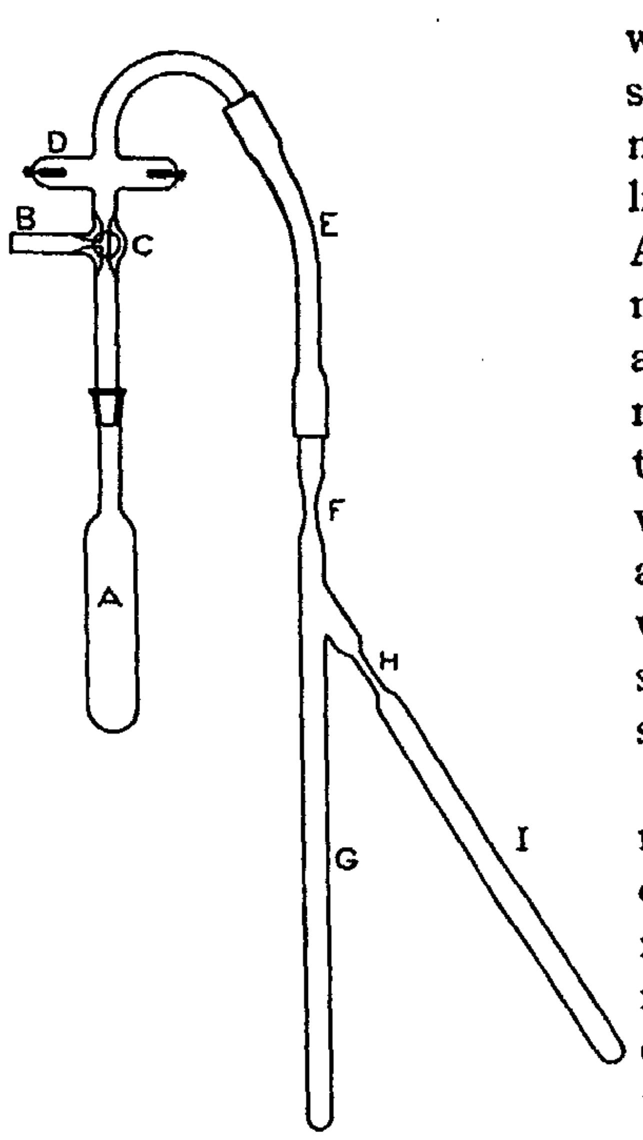

Fig. 1

Fig. 1 shows the apparatus used. From 0.04 to 0.08 gram of freshly scraped magnesium ribbon was placed in the glass tube I before drawing down at H. This was connected by the stout rubber tube E to the glass bulb A filled with fine granular wood charcoal. Through the tube B and the three-way stopcock C the whole apparatus was exhausted as far as possible with an ordinary water jet pump, the bulb A being heated strongly with a Bunsen burner. The water jet pump was then

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[1] Hasslinger, R. v. and Wolf, J.: Monatsheft für Chemie, 23, 817–822 (1902); 24, 633–647 (1903).

shut off by rotating C a half turn, and as soon as A cooled to room temperature it was immersed in liquid air. By connecting the metallic terminals in D to an induction coil the vacuum produced by the absorption of gas in the charcoal[1] could be easily judged from the character of the discharge. When the green fluorescence characteristic of high vacuum appeared, the tube I was heated with a burner as strongly as possible without softening the glass. The appearance in D clearly indicated the liberation of gas under this treatment although no appreciable change in appearance or weight took place in the magnesium ribbon. With powdered magnesium in some of the early experiments the gas current was so strong as to blow the fine particles of the metal over into the pump. Slight as was the amount of gas removed from the metal, the treatment aided greatly in ensuring the subsequent action of the acetylene. Tubes given this treatment never failed to react promptly, while exactly similar preparations where this treatment was omitted only entered into reaction days or weeks after their preparation and some have now stood for several years without reacting appreciably.

When the tube I had cooled, connection was broken with the rubber tubing, G was half immersed in liquid air and first acetylene and then ammonia (both as gases) passed in through a narrow delivery tube until the desired amount of each had collected. While the mass was still frozen solid a small amount of magnesium or sodium or some of their carbides from a previous experiment was added to G. Connection was again made with the charcoal pump and with G still immersed in the liquid air, a vacuum corresponding to a few hundredths of a millimeter of mercury or less established, and the tube sealed off at F. The ammonia gas was drawn from a small steel cylinder charged with a good quality of commercial liquid ammonia and a few pieces of metallic sodium as dehydrating agent. Between this cylinder and the delivery tube was inserted a glass tube packed with alternate layers of quicklime

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[1] Dewar: Chem. News, 94, 173–175, 185–188 (1896).

and ignited asbestos. The acetylene generated from commercial calcium carbide and stored over water in a gas holder passed from thence through calcium chloride and phosphorus pentoxide, drying tubes to the delivery tube. Early experiments with more elaborate purifying apparatus showed no difference in the results and were discarded for the bulk of the work as unnecessary for the purpose in hand.

Upon thawing out G the metal or carbide in this limb underwent reaction with whatever moisture had found its way in, producing a flocculent mass of hydroxide. The limb I was then cooled and part of the contents of G distilled over into it, washed about and run back into G. Finally, the total liquid contents of G were distilled over into I, the latter frozen solid with liquid air and sealed off at H. Upon allowing I to thaw out and attain room temperature, a steady and vigorous action upon the magnesium almost always set in within a few minutes. Clouds of fine bubbles arose and the ribbon soon became covered with a white crust whose thickness grew to a maximum of about 2 mm or 3 mm by the time the last of the metal disappeared. This usually required from a quarter to half an hour. The use of magnesium powder in place of ribbon increased the velocity of the reaction so that the temperature rose rapidly and even with external water cooling several violent explosions of tubes resulted, one completely shattering a plate glass screen 8 mm in thickness. When the magnesium was in several pieces the action would often begin on one of these and continue for some time before the others became visibly affected, but if other pieces were brought in contact with this one by tipping the tube, action rapidly spread to them, suggesting the phenomena of the passive state, which has already been reported for magnesium in aqueous solutions.[1]

If, after the disappearance of the metal, the tube was left undisturbed for some hours, the white crust underwent a complete recrystallization into large, colorless, transparent

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[1] Baborowsky: Zeit. Elektrochemie, 11, 456 (1905).

crystals, many of which were perfectly regular tetrahedra, though many appeared to show other forms as well in combination. If the removal of moisture from the liquid in the limb G had been complete, the liquid remained perfectly clear; but the slightest trace of moisture produced separation of flocculent hydroxide. The solubility of the crystals in the liquid is very small indeed.

After the contents of the tube had undergone thorough recrystallization, the whole was again frozen, a scratch made on the portion H, connection made by means of rubber tubing with a gas-holder full of water, and as the tube began to thaw out and develop pressure, the tip was broken off at the scratch within the rubber connection. The excess of ammonia was quickly absorbed by the water of the gas-holder and the excess of acetylene by subsequent treatment with ammoniacal cuprous chloride solution. The greater part of the residual gas proved to be ethylene and was absorbed by fuming sulphuric acid. The residue from this treatment was passed through a small U-tube cooled in liquid air which effected the condensation of a portion of it. What passed through was practically pure nitrogen undergoing no change in passing over hot copper oxide and subsequently caustic potash.

The contents of the U-tube upon evaporation and analysis proved to be ethane. The volume of this latter gas varied in different experiments from about an eighth to a twelfth that of the ethylene. Owing to the solubility of the gases in the water of the gas-holder these results can only be considered as approximate and in all probability the proportions vary greatly with the conditions of experiments, such as concentration of acetylene, temperature of reaction, etc. The residual nitrogen usually amounted to several cubic centimeters and seemed rather greater than was likely to have come from accidental introduction of air during the manipulations. It may, however, have been dissolved in the acetylene and ammonia during their liquefaction. In one tube where the action had been particularly vigorous and the solid had caked, it was thought that a trace of hydrogen was detected. The analysis of the gases was only carried out to characterize the reaction products qualitatively. Moissan found in the corresponding reactions with the alkali and alkali earth metals[1] that the hydrogen displaced by the magnesium reacted quantitatively with excess of acetylene to form pure ethylene and nothing else. It seems quite probable that the presence of a metallic surface in the one case and the difference in temperature and pressure at which the two reactions were carried out, may account for this difference in type, especially as elsewhere Moissan[2] states that dry potassium liberates hydrogen when reacting with acetylene at room temperature.

Returning now to the subject of the crystalline product of the reaction, it was found that, after the last of the ammonia had evaporated, the crystals retained their perfect transparency and no further gas was given off as the temperature of the tube gradually rose, until +2° C was reached. At this point liberation of ammonia set in quite sharply. On cooling to 0° reabsorption took place. If from this point the temperature was allowed to rise quickly to that of the room, the ammonia became contaminated with considerable acetylene, the quantity of the latter varying with the rate of heating. If, however, the temperature of the room was only slowly attained (in the course of several hours) the ammonia did not contain more than 1 or 2 percent of acetylene, some of which probably came from minute liquid occlusions within the crystals.

The residual solid may then be heated up to a little over 60° C before appreciable quantities of gas are again given off. Between 60° and 65° a second liberation begins, not as sharply as the former one, and increases in velocity up to about 90° or 100°, at which temperatures it is practically completed in a few minutes. The gas given off is a mixture of ammonia and acetylene, its composition varying with the rate of heating, but, under ordinary conditions, averaging about 2 vol. NH_3 to 3 vol. C_2H_2. The solid lumps of the compound remain

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[1] Moissan: Comptes rendus, 127, 915 (1898).

[2] Ibid., 126, 302 (1898).

white pseudomorphs of the original crystals. Some of this material was further heated in a glass tube immersed in a bath of fused sodium and potassium nitrates, the temperature being observed on a Le Chatelier thermocouple pyrometer. Up to 400° C little or no visible change took place, as the temperature rose (at the rate of about 2° or 3° per minute). Above this temperature the mass began to darken. By the time 425° was reached it was a slate gray and at 450°, entirely black.

After several unsuccessful attempts to weigh out portions of the crystalline product stable at 0° and to effect its analysis by the usual methods, the following procedure was adopted as the only one giving reasonably concordant results. The material loses ammonia and acetylene so readily and is so extremely sensitive to moisture that any attempt to divide a single preparation into separate portions for analysis was abandoned. The tube of crystals made from accurately weighed amounts of magnesium ribbon was brought to 0° C as described above and left in the ice bath until no further gas was evolved. The tip was then sealed in the blast lamp and the tube was removed from bath and weighed. The contents of the tube were shaken completely down into a compact mass at the bottom and the tube cooled for about half its length in liquid air, thus creating a vacuum within. A small rubber tube provided with a pinch-cock and communicating with a bottle of 30 percent sulphuric acid was slipped over the capillary end, whose extreme tip was then broken off inside the rubber tube and the acid cautiously allowed to enter the tube at just such a rate that it reached nearly down to the mass of substance but did not touch it before solidifying completely. The tube was then filled about two-thirds full and its tip again sealed in the blast lamp. It was next allowed to thaw in a part-way inverted position, and finally the carbide gradually shaken down into the acid, care being taken not to hasten this process unduly, on account of the heat and pressure thus generated. Even with these precautions some tubes were lost by explosion at this point.

The substance went into solution and a crystalline precipitate of the double sulphate of magnesium and ammonium separated. When the action was complete, the tube was turned capillary end up, again frozen in liquid air, connected to a gas burette and allowed to thaw out. The liberated acetylene, after collection and measurement in the burette, had its purity checked by absorption in ammoniacal cuprous chloride solution. The sulphuric acid solution was washed out of the tube, and diluted up to 100 cc; 20 cc of this were used for ammonia determination by distillation with alkali and titration with standard acid. In a few cases the magnesium was also determined in this solution as pyrophosphate, but where no loss had occurred by spurting during the preparation of the crystals it was found more accurate to base the computations on the weighed amount of magnesium charged into the tube at the start.

Two analyses of the magnesium ribbon showed it to contain 98.9 and 98.6 percent Mg, respectively. Of the remainder, 0.2 percent was aluminum and the balance probably chargeable to alkali and alkali earth metals. The presence of nitrogen in the reaction gases already referred to, as well as the effect on the magnesium of heating in the vacuum, suggested the possibility that the metal might contain an appreciable amount of occluded gas. To settle this point some 2 grams of mercury and 0.0520 gram of clean magnesium ribbon were placed in a tube of 2.5 cc capacity which was then completely evacuated and sealed off. The mercury was next boiled gently for two or three minutes until it completely dissolved the magnesium and the whole was allowed to cool. The tip of the tube was then snipped off under mercury. The tube filled all but a small bubble whose volume was determined as 0.066 cc by weighing the tube in this condition and again when completely full of mercury. The quantity is of course too small to be of any significance in the present connection.

The result of the analyses as a whole is to fix the composition of crystals stable below 2° C as $MgC_2.C_2H_2.5NH_3$, as appears from the following data:

Tube No.	Mol. C_2H_2 per atom Mg	Mol. NH_3 per atom Mg
45	1.86	—
47	1.91	4.83
49	2.06	4.87
51	—	4.95

The acetylene in tube 49 was not measured directly but calculated from the total weight of the compound and that of the ammonia and magnesium. The volume of ammonia given off on slowly warming up the crystals from 0° C to room temperature, was measured in tubes 38 and 41 and found equivalent, respectively, to 1.52 and 1.48 molecules C_2H_2 per atom of Mg, this being confirmed in the case of tube 41 by direct determination of ammonia in the residue which gave 3.51 molecules of ammonia per atom of magnesium. The compound stable between 2° and 60° would therefore appear to be $(MgC_2.C_2H_2)_2.7NH_3$.

The peculiar relation between the acetylene and the ammonia liberated at higher temperatures finds its best explanation by analogy with hydrated salts of weak bases. For example, if we attempt to drive off the water of crystallization from magnesium chloride we obtain a mixture of water vapor and hydrochloric acid in varying proportions, depending upon the rapidity of heating and a more or less basic chloride is left behind, due to hydrolysis of the chloride by its water of crystallization. The present phenomenon is correspondingly the ammonolysis[1] of magnesium acetylide (or acid carbide) by its ammonia of crystallization.

An analysis of some of this product after heating at 150° was made early in the work (tube 20) before the method of

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[1] Cf. nomenclature of E. C. Franklin: Jour. Am. Chem. Soc., 27, 826 (1905).

preparation was fully in hand, but the results clearly indicate what had happened. The carbon was determined by measuring the volume of acetylene liberated by hydrochloric acid in an eudiometer tube, magnesium by addition of nitric acid and ignition to oxide and nitrogen by distillation with alkali and titration with acid. The result was

	Percent
Mg	45.5
N	44.3
C	3.7
H[1]	6.3
	Total, 99.8

This corresponds fairly closely to a mixture of 7.5 percent MgC_2 and 92.5 percent $Mg(NH_2)_2$. In other words, the carbide was over 90 per cent ammonolyzed in driving off the ammonia of crystallization. The residue, when strongly heated, gave off some ammonia mixed with much nitrogen and hydrogen, due undoubtedly to decomposition of the amide into nitride.

It seemed probable that if the ammonia could be driven off at a lower temperature, less of the carbide would be ammonolyzed. To accomplish this the following method was adopted: A tube of the crystals (No. 52) was prepared in the manner described above. This tube I (Fig. 2) was then sealed to a tube of charcoal, J, through the T tube, the open end of the T connecting with the rubber tube of the charcoal air pump (Fig. 1). Tube I was kept in a bath of ice water while the whole apparatus was exhausted as previously described in the preparation of the crystals themselves, the tube J being strongly heated during this procedure. The apparatus was then sealed off at L (Fig. 2), the tube J placed in a flask of liquid air and the tube I in an ice water bath and left over night to slowly warm up. Next morning the ice bath had reached a

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[1] Calculated for $Mg(NH_2)_2$ from observed N.

temperature of 9°. With the tube J still in liquid air tube I was next heated in an air bath together with a similar tube (No. 48) which was not connected to a charcoal pump but merely left open through a fine capillary to maintain atmospheric pressure. The temperature of the air bath was raised to 50° in the course of half an hour and a current of gas was seen to stir the contents of tube 52 very perceptibly. The temperature was then slowly raised during the next five hours to 145°, when tube 52 was sealed off at M and tube 48 was sealed at its open tip. Both tubes were then cooled and subjected to analysis in the way already described. In tube 48 the reaction of the solid upon the sulphuric acid was, as usual, vigorous but not explosive, while in tube 52 it was accompanied by a bright flash and a blackening of the contents of the tube, apparently from the decomposition of the acetylene with separation of carbon.

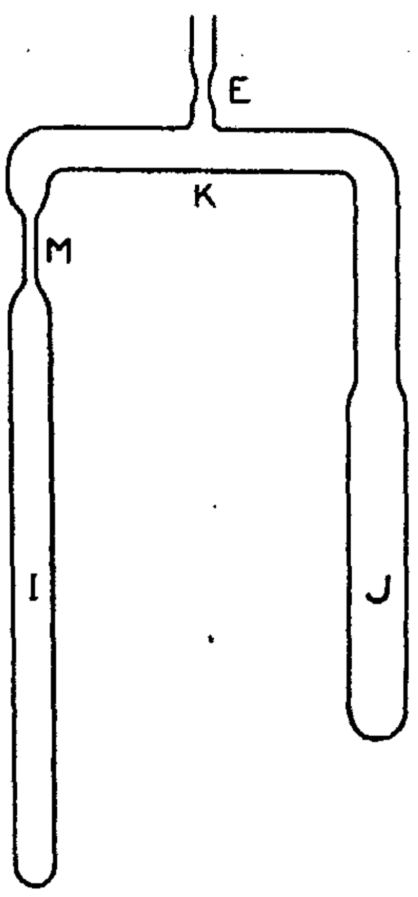

Fig. 2

Tube 48 was originally charged with 0.0558 gram of metallic magnesium and tube 52 with 0.0589 gram. From tube 48 only 7 cc of gas were obtained and of this over 1 cc was evidently entrained air, the rest being acetylene whereas had the magnesium formed pure carbide 54 cc of acetylene should have resulted. The ammonia determination gave 0.0542 gram nitrogen as against 0.0643 calculated for pure $Mg(NH_2)_2$. The sum of the carbon and nitrogen is here hardly sufficient to satisfy the whole of the magnesium unless some of the amide had already gone to nitride or traces of moisture worked in while the tube was heating in the air bath. However, the same preponderance of amide over carbide is here again illustrated as in tube 20. Tube 52, on the other hand, furnished 54 cc of gas as compared with 57 required by theory for pure MgC_2. Of these 54 cc only 9.7 cc were still undecomposed acetylene, the remainder being practically pure hydrogen, probably corresponding to the carbon which had been precipitated in a dense black mass throughout the tube. The ammonia determination gave 0.0083 gram N corresponding to about $^1/_4$ mol NH_3 to every atom Mg. The violence of the action makes it unsafe to lay too much stress on the quantitative interpretation of the volume of free hydrogen, but it is certainly evident that the vacuum treatment here greatly favored the formation of carbide at the expense of the amide—which was the object of the experiment.

Tube 54 was treated in the same manner save that the charcoal tube was started at a temperature of about 5° in place of 0° and this treatment continued, the temperature gradually rising to that of the room, during four days in place of simply over night. The analysis of the product showed about three-quarters of the Mg as carbide and the remaining quarter as amide, pointing to the conclusion that if carbide of higher purity than that from tube 52 is aimed at most of the ammonia must probably be removed at temperatures below 0° C.

By way of comparison the action of both liquid acetylene and liquid ammonia was tried separately on metallic magnesium. In the case of the pure acetylene no action whatever occurred although the glass tube containing the mixture has now been under observation for over seven years and lay for nearly a year exposed to direct sunlight where it was often above the critical temperature of the liquid (*i. e.*, 37° C.).

In the case of pure ammonia on the other hand, it was found, if the materials were dried with sufficient care, that the liquid soon took on a blue color which reached a fairly constant intensity within a short time, usually less than an hour. This has now persisted in one tube where magnesium ribbon was used, for over seven years, while most of the metal has gradually changed to a fine light gray, apparently amorphous powder. This reaction involves liberation of hydrogen as shown by opening the tubes after freezing. In the tubes where the metal was in the form of fine powder the blue color disappeared after some months, probably marking the final conversion of all the metal to amide. The tube, above mentioned as still showing blue color after seven years, was kept in a cool place most of the time which probably accounts partly for the difference in its behavior.

A tube (No. 25) charged with 0.1019 gram of very pure magnesium powder previously heated under high vacuum and a large excess of pure, dry ammonia retained its blue color essentially constant for about six months, at the end of which time the metal seemed to have been completely converted into the white powder, and the blue color disappeared. The tube was left for three months longer. The contents were then frozen in liquid air and an attempt made to collect and measure the hydrogen evolved but unfortunately upon breaking the capillary tip of the tube within the rubber connection to the gas burette, the sudden rush of compressed hydrogen burst even the heavy-walled rubber tubing used for the purpose and the gasometric determination was lost, a small amount (estimated at much less than 1 percent of the whole) of the solid which had lodged in the capillary was also lost. The tube was thawed out and the ammonia allowed to evaporate, leaving a fine, pure white powder weighing 0.22 gram as against 0.236 gram calculated for $Mg(NH_2)_2$ had the whole 0.1019 gram of metal been converted into this compound. The discrepancy may be accounted for over and above what was lost in opening the tube either by some of the metal having escaped complete reaction even in the time allowed or by presence of oxide and other impurities in the fine magnesium powder used. The agreement is considered, however, sufficient under the circumstances to justify the conclusion that magnesium behaves precisely like the metals of the potassium group, forming first the typical blue solution of the metal itself which then slowly decomposes into amide and hydrogen. It is evidently vastly less soluble as metal than any of the other alkali or alkali earth metals. The addition of platinum black to the tubes hastens the conversion to amide to some extent. A pair of platinum wire electrodes was sealed into one tube and when a current was passed through the liquid, blue streaks developed from the cathode and an almost microscopic tree-like growth of bright metal grew out from this electrode along the glass.

Although pure ammonia thus evidently does react with magnesium, the reaction is so slow a process that it can be entirely disregarded in comparison with the rapid and energetic reaction of the acetylene and ammonia mixture. It was found, however, that the pure amide from tube 25 added to the mixture of ammonia and acetylene underwent an almost instantaneous transformation to the crystalline acetylide with five molecules of ammonia described above. This naturally raised the question as to the state of the acetylene dissolved in the ammonia. Was it dissociating as an acid, and combining to form ammonium carbide or acetylide? If these compounds were formed in appreciable amounts we might with some confidence expect them to raise the conductivity of the ammonia. Accordingly a tube was prepared similar to that shown in Fig. 1, save that at the bottom of the limb I a pair of sheet platinum electrodes were sealed in, and no magnesium was placed in this limb. A strip of magnesium was however placed in G which was then charged with a mixture of about 1 part by volume of liquid acetylene to 4 parts of liquid ammonia. The tube was finally frozen, exhausted, and sealed at F in the usual manner. The resistance capacity of the vessel was determined before the final filling by measuring 0.02 normal potassium chloride solution in it which showed a resistance of 120 ohms at 23.7°.

Upon first distilling the mixture of acetylene and ammonia over from limb G to I it showed a resistance of only 4000 ohms at room temperature. It was washed back into G and allowed to stand several days in contact with the magnesium strip. The latter not having been previously heated in vacuum did not react with the mixture as in the tubes described in the first part of this paper, but only slowly tarnished on the surface. Every few days the liquid was distilled over again into I, its resistance measured with Wheatstone bridge and telephone at room temperature (15–19° C) and then poured back again into G. The resistance rose during a week to nearly 600,000 ohms and at the end of a month was over 1,300,000 from which the non-existence of any significant amount of ammonium carbide even in solution seems a safe inference.

To test the action of the mixture of acetylene and ammonia on other metals, tubes were prepared containing copper, zinc, and aluminum, but in no case can any action be noticed although these preparations are now several years old.

On the other hand, the solution in liquid ammonia of the solid colorless hydrocarbon fluoren $C_{13}H_{10}$ which like acetylene is known to have one hydrogen easily replaceable with metals, was found to react readily with metallic magnesium at room temperature giving a deep orange-red solution and a granular residue of the same color which later underwent partial recrystallization in the liquid, forming long needle crystals. This product and reaction have not been further investigated.

Summary

At room temperature liquid acetylene does not react with metallic magnesium but mixtures of liquid anhydrous ammonia and acetylene react fairly readily with the metal, forming the crystalline compound $MgC_2.C_2H_2.5NH_3$ and ethylene mixed with smaller quantities of ethane. Phenomena suggestive of a passive state of the metal are also noted in this connection.

This crystalline compound at +2° C under one atmosphere loses 1.5 molecules of ammonia. The resulting compound is stable up to 60° C when it loses both acetylene and ammonia leaving a mixture consisting chiefly of amide and nitride with a little carbide. This begins to blacken at about 425° C, evidently due to decomposition of the carbide into its elements. By the withdrawal of the ammonia from the original solid under high vacuum at low temperatures before heating, a nearly pure carbide may be obtained. At room temperatures liquid anhydrous ammonia dissolves metallic magnesium to a very slight extent, forming a faint blue solution which gradually decomposes into the amide and hydrogen in a manner analogous to the corresponding reaction of the alkali and alkaline earth metals.

Mixtures of liquid ammonia and acetylene do not show electrical conductivity comparable with solutions of the alkaline carbides or acetylides from which the non-existence of ammonium carbide or acetylide is inferred.

These mixtures at room temperature do not attack either zinc, aluminum, or copper.

A solution of fluoren $C_{13}H_{20}$ in liquid ammonia readily reacts with magnesium at room temperature.

Berkeley, Calif.,
October, 1913

MOLECULAR ATTRACTION. X. A REPLY TO CRITICISM

BY J. E. MILLS

The primary object of this paper is to reply to an article by Dr. A. P. Mathews[1] containing a discussion of the author's views and work on molecular attraction.

The articles which I have published[2] on molecular attraction and related subjects were written as the work proceeded. These papers are now being revised but the revised work is not suitable for publication in a journal. Therefore a reply here.

First. The Correctness of the Fundamental Equation,

$$1. \quad \frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant, or } \lambda = \mu' (\sqrt[3]{d} - \sqrt[3]{D}),$$

has been brought into question.

Here L is the heat of vaporization of 1 gram of the liquid, E_E is the energy spent in overcoming the external pressure as the liquid expands to the volume of the saturated vapor. $L - E_E$ is therefore the so-called internal heat of vaporization and is called λ. d and D are the densities of the liquid and saturated vapor, respectively, at the temperature of the vaporization. The constant given by the equation I have called μ'.

A summary of the evidence is given in the papers cited, particularly Jour. Phys. Chem., 13, 512 (1909) and Phil.

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[1] Jour. Phys. Chem., 17, 520 (1913).

[2] Ibid., 6, 209 (1902); 8, 383, 593 (1904); 9, 402 (1905); 10, 1 (1906); 11, 132, 594 (1907); 13, 512 (1909); 15, 417 (1911); Jour. Am. Chem. Soc. 31, 1099 (1909); Phil. Mag., Oct. (1910); July (1911); Oct. (1912); Trans. Am. Electrochem. Soc., 14, 35 (1908); Chem. News, 102, 77 (1910); and related papers, Mills and MacRae: Jour. Am. Chem. Soc., 32, 1162 (1910); Jour. Phys. Chem., 14, 797 (1910); 15, 54 (1911).

Mag., July (1911) and Oct. (1912). Mathews,[1] after stating that the equation gives a constant except in the neighborhood of the critical temperature, says that I "ascribed the fall of the constant near the critical temperature to the inaccuracy of the data." This statement is misleading. *What I did was to prove beyond any question that the Biot formula used to calculate the* $\frac{dP}{dT}$ *necessary in calculating the latent heat did not correctly represent the observed data,* and that the deviations were practically always in a definite direction causing the constant given by the equation to be too low near the critical temperature. This fact must be admitted by anyone who attempts to make the Biot formula fit the observations. It simply will not fit near the critical temperature.

Now for the three substances where more direct observations of the $\frac{dP}{dT}$ were obtainable at the critical temperature, equation 1 showed agreement to within the limit of error of the measurements. Without going here into evidence formerly published in part, and later to be published in full, I will only say that there is no evidence to show, and no reason to suppose, that equation 1 is not exactly correct at the critical temperature for non-associated substances. There is, moreover, strong evidence to show that it is certainly correct, even at the critical temperature, to within 2 percent for non-associated substances.

The observations of Young and his co-workers are remarkably correct and I have often expressed my admiration of their work. The fact that these observations permit of a universal accuracy in the constant only to within 2 percent

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[1] Dr. Mathews writes, "If you have read my last paper (Jour. Phys. Chem., Oct., 1913) you will have noticed that I there accept your equation, $\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}}$ = constant, as probably correct clear to the critical temperature. You think that Biot's formula gives incorrect results close to the critical temperature, and in this I think you are right; at least I wish that you may be right. Were I rewriting my paper which you answer I should change this part of the paper, which after all was a very subordinate point," etc.

is due largely, as often explained before, to an enormous multiplication of error in the necessary calculations. Yet in spite of this multiplication of error only 17 values of the constant out of 431 for 25 substances, diverge from the average value (except at 0° C and near the critical temperature for explained causes) by more than 1.5 percent.

The statement made by Mathews[1] that "in ether and ethyl acetate there is a pretty steady fall in the constant throughout" is correct as regards ethyl acetate and wrong as regards ether.[2] I quote further from Mathews:[3] "The apparently negative value of b_v is found closer to the critical temperature in the esters which are known to associate slightly." I also believe that there is slight association in the esters and that the constant of equation 1 for them should decrease slightly with the temperature. But after allowing for the known sources of error and considering the esters as a whole such decrease must be slight, probably not more than 2 percent, and therefore within, or so nearly within, the error of the observations as used, as to render a certain statement impossible at this time. The best evidence upon this point comes from a comparison of equation 1 with Dieterici's equation at the critical temperature,

$$2. \qquad \lambda = \mathrm{CRT}\, ln \frac{d}{\mathrm{D}}.$$

For the esters there is a divergence shown on comparison of the two equations at the critical temperature ranging from 2.2 percent with methyl formate, to 4.5 percent with propyl acetate. Probably at least half of this divergence is due to Dieterici's equation which is also affected by molecular association, and some of it seems certainly due to another known source of error.

Second. Van der Waals' Equation.—Much of Mathews' article consists in a more or less direct judgment of the fundamental equation 1 and derived conclusions from the stand-

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[1] Loc. cit., p. 524.

[2] Jour. Phys. Chem., 13, 518 (1909).

[3] Loc. cit., p. 526.

point of van der Waals' equation and views. Van der Waals' equation is not correct, and it is not only not correct, but it is nowhere near correct when viewed as a whole. Dieterici expresses exactly my own attitude toward van der Waals' equation when he says,[1] "Nach der Nobelpreisrede[2] von van der Waals ist est nicht mehr nötig, auf die schwachen Punkte in Studium dieser Zustandsgleichung aufmerksam zu machen; viel näher liegt es, die Frage, die van der Waals selbst aufwirft, 'gibt es einen besseren Weg?' zu verfolgen." Mathews himself confesses to the situation when he says, on page 530, "As a matter of fact $L - E_E \Big/ \left(\frac{1}{V_1} - \frac{1}{V_v}\right)$ (from van der Waals' equation, J. E. M.) *does not equal a constant*, hence our assumption must be wrong. But if the assumption is wrong then the fact that $L - E_E \Big/ \left(\frac{1}{V_1{}^{1/3}} - \frac{1}{V_v{}^{1/3}}\right)$ *happens to equal a constant* cannot be adduced as evidence that molecules attract inversely as the square of the distance." (Italics mine, J. E. M.) I will not, therefore, follow Mathews' discussion in detail. My own equation and views could not be correct if they agreed with van der Waals' equation in its usual form, and I pointed out, at the end of my first paper in 1902, "that the law of attraction assumed does not lead to the equation of van der Waals'." When any one has succeeded in modifying van der Waals' equation so as to make it correctly represent the facts, then perhaps my equation and views will not be found irreconcilable.

Third. The fundamental equation not empirical.—Mathews, in several places, refers to equation 1 as an "empirical relationship." A little history will perhaps be pardoned as it will serve to bring out several facts clearly.

The fundamental equation, $\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}}$ = constant, was not derived as an empirical equation in the usual sense of that

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[1] Drude's Ann., 35, 220 (1911).

[2] Van der Waals: "Die Zustandsgleichung," Leipzig Akadem. Verlagsges. (1911).

term. When an undergraduate in college on working out a problem in calculus involving the velocity, and hence the energy, of a cannon ball shot upwards from the earth, the idea occurred to me that possibly the much desired law of molecular attraction could be found by a similar process. I asked two of my instructors at that time, without stating the reason for the question, if there "was any reason for supposing the energy *per se* of the molecules of a liquid and its vapor to be the same, or any method for arriving at the energy *per se* of the molecules of the liquid?" Of course the information desired was unknown. But this first step will surely make clear the fact that I could never later have overlooked the fundamental importance of the question as to the relative energy of the liquid and vapor molecules in obtaining the law of attraction. (See later.) It was perhaps five years afterwards when I obtained some idea as to the correct answer to the question above stated and only then did I even attempt the next step. Meanwhile, I was interested in the cause of gravitational and chemical attraction, and it is interesting to myself at least, that during that time I recorded in an old note book on the subject a suspicion as to the correctness of the *numerator factor* of Newton's law of gravitation.

The next step in the discovery of this "empirical equation" came when I recognized the fact that Watterson's equation,

3. $$\frac{\sigma_p}{\sigma_v} = \gamma = \frac{E_K + E_I + E_E}{E_K + E_I},$$

could be combined with the equations derived also from the kinetic theory and facts of gases

4. $$E_K = {}^3/_2\,R,$$

5. $$E_E = R,$$

for a difference in temperature of one degree, and written,

$$\gamma = \frac{{}^3/_2\,R + E_I + R}{{}^3/_2\,R + E_I} = \frac{{}^5/_3\,R + E_I}{{}^3/_2\,R + E_I}, \text{ or}$$

6. $$E_I = \frac{R}{2}\,\frac{5 - 3\gamma}{\gamma - 1} \text{ or from 4}$$

7. $$E_I = \frac{{}^5/_3 - \gamma}{\gamma - 1}.\,E_K.$$

In these equations σ_p and σ_v are the specific heat at constant pressure and constant volume of a gas. E_K is the kinetic energy of the molecules, E_I is the internal energy of the molecules (best defined from the equation $\sigma_v = E_K + E_I$) and E_E is the energy spent in overcoming the external pressure of the gas during expansion.

In words equation 7 means that for a perfect gas *the internal energy of the gas is proportional to the kinetic energy of the gas.*

Now I believe, and there is reason for the belief, that in the molecules of a liquid similarly, the internal energy E_I was proportional to the kinetic translational energy E_K.

The third step came practically at the same time when I recognized that the fact that cane sugar molecules dissolved in water caused an osmotic pressure similar to a gas pressure, indicated that the cane sugar molecules were behaving like gaseous molecules in part at least. This indicated a translational energy similar to the gas translational energy. The water molecules must have the same translational energy as the dissolved cane sugar molecules, a conclusion already drawn by Ostwald. The internal energy of the water molecules was, from equation 7, probably proportional to their translational energy. In short, it seemed that the molecular energy *per se* of molecules of a liquid and its vapor at the same temperature must be the same.

The same night that I reached this conclusion—the answer to my old question—I attacked the problem of molecular attraction, paralleling the cannon ball problem, and reached the fundamental equation essentially as stated in equation 1, without one particle of experimental evidence. The first experimental evidence in its favor was obtained that same night.

In obtaining the equation I assumed that the molecular attraction varied inversely as the square of the distance apart of the molecules. This seemed to me the most probable assumption for several reasons—primarily perhaps because the other attractive forces whose laws were known, magnetic, electrical, and gravitational, varied in that way, and I suspected a close relationship among these forces. But also because any emanation or disturbance proceeding from a center seemed to me necessarily to be compelled to have an inverse square law of distance as *one of its factors.* Because I did not know the other factors, or the influence of temperature, I did not feel at all certain that the deduced equation would prove true, and intended to try other laws of force and modifications if the equation failed. *The equation proved true.* Moreover it is the only equation concerning molecular attraction that ever has proved true. It is rather important, therefore, to look carefully into the reasoning by which it was deduced before rejecting that reasoning.

Fourth. The role of mass in molecular attraction.—A little more history will help to throw light upon the equation. When sufficient experimental proof had accumulated to convince me that the equation was true, I set eagerly to work to extend the results in three directions. First,[1] I investigated the attraction itself, rather expecting the molecular attraction to behave as does the gravitational attraction as regards mass, having temporarily overlooked my suspicion above referred to of the gravitational law. I readily found on trying to compare the attractions of, let us say, oxygen molecules with carbon dioxide molecules (I have forgotten the gases actually used, I compared several I think) that these attractions did not vary as the masses of the molecules. Somewhat surprised, I contented myself with the statement made at the end of the first paper, "*The molecular attraction appears to resemble the attraction of gravitation in that it varies inversely as the square of the distance apart of the attracting molecules and does not vary with the temperature. It differs from the attraction of gravity in being determined primarily by the construction of the molecule and not by its mass.*"

I never myself forgot that statement, nor intended to

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[1] The other investigations dealt with specific heats and the equation of state.

change it. Some subsequent rather carelessly worded statements of mine mislead others. Thus it will be seen that the first idea that I obtained as to the true relation of mass in molecular attraction had nothing whatever to do with the correctness of the equation. Mathews says[1] "That Mills' expression, $\mu'\left(\frac{1}{V_l^{1/3}} - \frac{1}{V_v^{1/3}}\right)$, does not represent the work done in overcoming molecular cohesion may be shown, also, if the attempt is made to deduce the formula on this basis, assuming the attraction to vary inversely as the square of the distance. A value is obtained for μ' widely different from that found. Mills realized this difficulty and tried to avoid it by assuming that the law that matter attracted itself as the product of the masses was incorrect." This statement hardly expresses the situation correctly and the facts cannot be disposed of so briefly.

In the sixth paper[2] I corrected an error made in the derivation of the fundamental equation from the assumed law of attraction,

$$8. \qquad f = \frac{\mu^2 m^2}{s^2},$$

obtaining as the complete expression,

$$9. \qquad \frac{M(L - E_E)}{\sqrt[3]{d} - \sqrt[3]{D}} = \frac{M^2\mu^2 C}{n^2\sqrt[3]{m}} = m^{5/3}\mu^2 C,$$

where n is the number of molecules in a gram, m is the molecular weight, $nm = M$, and C was a constant only when the number of molecules was constant. For a constant mass the equation reduces to the form previously given in this paper,

$$1. \qquad \frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}.$$

Now one has a perfect right to start with a constant mass and to continue the investigation with a constant mass. By so doing one will obtain for μ' exactly the values given as proof of equation 1. The statement of Mathews that by using the

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[1] Loc. cit., p. 530.

[2] Jour. Phys. Chem., 11, 132 (1907).

gravitational law of force, equation 8, "a value is obtained for μ' widely different from that found" is therefore misleading. The gravitational law of attraction produces equation 1 by the *strictest* mathematics if we deal always with the same mass originally used on starting the investigation. To make this point doubly sure I used[1] Helmholtz's equation for the heat given out by the contraction of the sun under gravitational attraction and showed that this equation, obtained by a totally different mathematical treatment, also reduced to the form of equation 1 for a constant mass. But, *vary the mass and the equation shows that the heat given out should vary as the 5/3 power of the mass.* Now we know as a matter of fact that the heat of vaporization of 2 grams of liquid is just twice the heat of vaporization of one gram of liquid and not $2^{5/3}$ times as much.

In other words, the important fact is that the gravitational law of attraction applied to molecular attraction gives a true equation if we keep the mass investigated constant, which we have a perfect right to do; and gives a false equation if we allow the mass under investigation to vary, which we have an equal right to do. I would write these words in capitals if that would serve better to focus attention upon the fact they set forth.

It seems so clear to me, without mathematics, that, if a variation in the *mass* of liquid taken causes the difference above mentioned, the trouble is due to the numerator factor of the above assumed gravitational law of force (the only part concerned with mass), and not to the denominator of the law (which is concerned with distance apart only), that I cannot realize where the doubt expressed by others can creep in. Mathematically, it is easy to show that an assumed law of molecular force,

$$f = \frac{\mu m}{s^2}, \tag{10.}$$

will give an equation,

$$M\lambda = M\mu'(\sqrt[3]{d} - \sqrt[3]{D}), \tag{11.}$$

equally true for a constant or for a variable mass.

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[1] Jour. Phys. Chem., 11, 147 (1907).

My assumption that matter (molecules) did not attract as the product of their masses was made for the compelling reasons set forth above, and not as alleged by Mathews to account for variations in μ'. I now realize that this conclusion was foreshadowed by the investigation so briefly reported in the first paper as indicating that "molecular attraction is determined primarily by the construction of the molecule and not by its mass," and that it receives further support from many facts dimly recognized even before the fundamental equation was discovered.

Fifth. Is the internal heat of vaporization spent solely in overcoming molecular attractive forces?—A rough copy of my first paper contained a good deal about specific heats. Before publishing it I discovered that my ideas regarding the specific heats were not in accord with the facts. I therefore eliminated from the paper all discussion of specific heat and contented myself with the statement made at the end of that paper, "The argument pursued might lead one to suspect that the entire increase of the specific heat of a liquid over that of a gas at constant volume must be spent in increasing the distance apart of the molecules. Investigation shows that this is not always, if it is ever the case, and herein possibly lies the true cause of the discrepancies from the theory." The true cause of the discrepancies referred to were later in all cases discovered and had nothing to do with the specific heat problem. A reviewer of the first paper criticised it for not pointing out certain simple specific heat relations which should follow. The truth is that the simple specific heat relations that I had expected did not follow. I did not know, at the time of publication of the first paper, that specific heat relations could be shown to contradict the belief that the energy of the molecules of a liquid and its vapor were the same, but I discovered the fact later and in the sixth paper (1907) stated,[1] "As regards now the first step—the equality of the energy *per se* of a molecule of a liquid and

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[1] Loc. cit., p. 156.

of a molecule of its vapor—we have already stated in outline the facts which lead us to that belief. This first step is the most fundamental and important step in our work and is the most open to doubt. The fact that using this belief as a basis we derived an equation that appears to be true, is perhaps again the best evidence that the belief expresses, at least partly, the truth. But only in part, for in attempting to derive a direct method for testing this belief we find that it will require some modification. An account of this work could not be introduced within the limits of this paper and we hope shortly to publish this investigation in a separate article. Recognizing the doubt, we would state that any errors introduced by our statement have undoubtedly canceled, since one is certainly able to calculate the energy given out by the contraction of a vapor into a liquid from the same formula used to calculate the energy given out by the contraction of the sun." Surely this statement is evidence sufficient to show that after I recognized the fact that the energy *per se* of the molecules of a liquid and its vapor were not the same, the fact was not concealed. And I will repeat again that Mathews is exactly right in his belief that the energy *per se* of the molecules of liquid and vapor are not the same. I reached this conclusion by the simple process of adding up all of the energy added to a substance from the absolute zero to its condition as liquid. That is, I summed up the specific heat energy added and the latent heat of fusion. Then, allowing for the energy necessary to produce the slight expansion of the solid and liquid (this can be done either from my own theory or thermodynamically), I compared the remainder with the energy which the substance would have as a perfect gas at the given temperature. The result shows that the molecules of the liquid have *per se* far more energy than the molecules of the gas are popularly supposed to possess. So very much more that it was fruitless to consider the difference as by any possibility due to the experimental uncertainties which are usually large. By this time (probably 1906) I had accumulated so much evidence as to the truth of the fundamental equation that I myself placed absolute confidence in its correctness. Moreover, the argument quoted above, involving the osmotic pressure of cane sugar molecules, was even stronger than before, the excellent work of Morse and his co-workers having begun to appear. I contented myself therefore with the paragraph already quoted from the sixth paper and set about a study of the situation.

An enormous amount of data on specific heats was collected, sifted, and studied. I thought at first that the trouble might lie with our ideas of temperature (which do require clarification). Then since the facts apparently indicated that always when particles were closer together they, in some way, retained or possessed more energy, I considered the possibility of a change of inertia (mass). This supposition is not so easy to reject in view of the facts as one might suppose. I was aware of T. W. Richards' work upon the compressibility of the molecules, and the possibility that molecular expansion would require energy. For several years nothing was published on the subject because I could not even satisfy myself. Finally light began to dawn upon the situation and I recognized that *the gravitational law of attraction necessitated that whenever two bodies came together from an infinite distance and formed a stable system of moving bodies that these bodies retain exactly as much energy as they gave out.* The law of gravitation necessitates the *retention of energy* in a stable system of moving particles just as much as it *necessitates the giving out of energy* when the stable system is formed.

When I did recognize the above fact I found it very much more difficult than one would suppose (since the problem of two bodies under gravitational attraction had been completely solved) to give the exact mathematical proof of the statement finally made,[1] "*The energy given out by any two bodies originally at rest at an infinite distance apart in forming any stable configuration (circular, elliptical, or limited linear orbit) under the action of gravitational attraction is equal to the kinetic*

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[1] Phil. Mag., July, 1911, p. 105. This paper also contains the proof of the statement.

energy which they retain, and is, for either body, inversely proportional to its mean distance from their common center of mass."

In the paper referred to, I was unable to extend this conclusion to *n* particles as a mathematical proposition. During the last summer I have extended the proof to *n* particles and shown that this proof holds for the molecular law of attraction. This work has not yet been published.

Mathews has this to say[1] regarding this phase of my work, "While Mills states, in a recent paper, that not all the internal heat may be used in doing this work, and attempts to show that this is not incompatible with this conclusion, the conclusion nevertheless depends on the assumption that it is so used and that there is no change in the internal energy of the molecules on passing from the liquid to the vapor. It is clear that if this premise be not true, then the conclusion does not follow." "This premise I believe to be certainly erroneous."

The premise certainly is erroneous as I pointed out six years ago in the quotation given above. *It is in fact a contradiction of the law of attraction assumed.* The law of attraction assumed compels the freely moving molecules of the liquid to retain a given amount of orbital energy absolutely as much as it compels energy to be given out on the approach of the molecules. When the freedom of motion of the liquid molecules is checked, then some of this orbital energy which they retain is given out as latent heat of fusion. Some more of it is probably given out as the temperature is lowered. I doubt if all of it ever is surrendered even at the absolute zero. (See later.)

The moon is obliged to retain a given amount of energy as orbital energy if it is to continue in its orbit about the earth. It retains as a matter of fact exactly as much energy as it gave out when assuming that orbital position. How it happens that "all of us" scientists have considered the particles of a liquid to be freely moving under an attractive force and have failed

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[1] Loc. cit., p. 524.

to consider the obvious fact that they must retain orbital energy is hard to see.

Of course, since this retained orbital energy is due to the attractive forces, I was, throughout all of my previous papers, really dealing with one-half of the result of the attractive force instead of with the total result as I had supposed.

Sixth. The volume actually occupied by the molecules and the change of this volume with temperature and pressure.

In the article cited on Chemical Energy[1] I have given the data to prove the statement that "*The 16 grams of oxygen and the 2.016 grams of hydrogen together at —273° C occupy 34.78 cubic centimeters, and when occupying this volume at that temperature they contain 67,300 calories more of energy than do the 18.016 grams of ice which they form if united, and which occupies a volume of 19.21 cc.*

No supposition and no uncertainty whatever is involved in this statement except the slight uncertainty of the measurements. More accurate measurements are now available but the result is not materially changed.

There is a good deal of food for thought in the above facts. In the first place we have no evidence whatever as to the energy retained by the molecules of the water at 0° absolute. Patterson[2] estimates the potential energy of charge on 16 grams of oxygen and 2.016 grams of hydrogen at 640,000 calories and Arrhenius[1] at 636,100 calories, both on the basis of the electron theory. At any rate, we can content ourselves with the statement that the energy retained by the molecules of water at 0° absolute may be very large. We do know positively that the oxygen and hydrogen at that temperature possessed 67,300 calories more of energy than does the 18.016 grams of water which they form if united. Now in what form is that energy? It has been pointed out long ago, by Clausius I think, that under Newtonian mechanics, energy cannot be retained in a system wholly as kinetic or wholly as potential.

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[1] Trans. Am. Electrochem. Soc., 14, 35 (1908).

[2] Chem. News, 102, 77 (1910).

energy, but must exist partly as kinetic energy and partly as potential energy. This being true, one is compelled to conclude that the oxygen and hydrogen molecules (or parts of molecules) must be in motion with terrific speed even at the absolute zero. I, at least, have never been able to escape this conclusion, and I think the atoms of hydrogen and oxygen in water, and the atoms of other compounds travel at great speed. We get some evidence of this sort of activity in radium and radioactive compounds.

If when we talk about the "real" volume occupied by molecules we mean the volume taken up because of these motions, I have no objection to the phrase, and if, when we speak of the compressibility of the atoms and molecules, we have in mind the compression of these rapidly moving parts closer together, I again have no objection to the idea. I do object to all ideas which leave out of consideration the atomic and interatomic motion. My position as to the necessity of considering such molecular volumes, or molecular changes in volume, in studying molecular attraction can now be understood.

The energy relations of the heavenly bodies have nothing to do with the volume occupied by the heavenly bodies but are determined by their attractions. Now in my work upon molecular attraction I have been considering energy relations, and these energy relations are similarly determined by attractive forces which have nothing to do with volumes as above defined. The influence of volume is brought into play only when freedom of motion is destroyed.

The internal energy of atoms changes with the temperature. But in nearly all of my published work I have been dealing solely with the energy of vaporization and *here the temperature is precisely the same before as after the expansion.*

It will again be argued that the change of internal energy with temperature must alter the molecular attraction. I think this is true. But the alteration for the chemically stable substances studied throughout the range of temperature studied is very small. Suppose 18.016 grams of water really represents some 640,000 calories of energy as hinted. The addition of a few hundred calories of energy within the atoms as the temperature is raised does indeed alter the molecular attraction somewhat but not greatly. It would alter the attraction greatly if the temperature range were continued to 1800° C. Perhaps by some such study one might finally prove that molecular attraction was only the "left over" chemical attraction. Mathews' remarks, as to the influence upon molecular attraction of valence and number of atoms, are interesting in this connection.

Mathews thinks that changes of pressure would also cause changes in molecular volume. Perhaps so, but it must be remembered that *there is no change in external pressure during vaporization.* The changes in internal pressure, caused by the attractive forces, are precisely what the calculation of the attraction takes into account, if you choose to look at it in that way.

After all, Mr. Mathews' views are closely akin to my own. He thinks magnetism and molecular attraction closely related and magnetic attraction is popularly supposed to follow an inverse square law. Also he quotes somewhat approvingly the idea that molecular cohesion is delimited by the surrounding molecules. But this idea is practically nothing more than putting into words the numerator factor of the proposed molecular law.

Summary

(1) It is shown that the decrease shown by the constant of the equation, $\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}}$ = constant, near the critical temperature was not attributed to errors in the observations used, but to the fact that the Biot formula used did not, and could not be made to represent the observations correctly.

(2) Emphasis is laid on the fact that my equation and views could not agree with the equation of van der Waals if mine were correct, since van der Waals' equation, in its present form, is known not to represent the facts accurately.

(3) Attention is called to the fact that the above equa-

tion is not an "empirical equation" but was derived theoretically by an argument still worthy of careful consideration. Afterwards the equation was proved from the experimental data.

(4) It is shown that the idea that the molecules did not attract as the product of the masses was introduced because of the important fact that "the gravitational law of attraction applied to molecular attraction gives a true equation if we keep the mass investigated constant, which we have a perfect right to do; and gives a false equation if we allow the mass under investigation to vary, which we have an equal right to do."

(5) It is pointed out that both the law of gravitation and the law of molecular attraction given, necessitate the retention of energy in a stable system of moving particles just as much as they necessitate the giving out of energy when the stable system is formed.

(6) Reasons are given for believing that it is not necessary to consider molecular volumes or changes in molecular volumes, in the interpretation of the fundamental equation,

$$\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant.}$$

University of South Carolina,
Columbia, S. C.
October, 1913

THE THEORY OF DYEING. II

BY WILDER D. BANCROFT

In order to get the maximum adsorption of a basic dye we should have present an ion of the opposite charge which is readily adsorbed. We therefore deduce the following conclusions in regard to a basic dye.

1. The dye is taken up most readily in an alkaline solution but may be taken up in a neutral or acid solution.

2. A readily adsorbed anion increases the amount of dye taken up.

3. A readily adsorbed cation decreases the amount of dye taken up.

These generalizations can easily be confirmed by means of Pelet-Jolivet's experiments with methylene blue. The effect of acidity and alkalinity are given in Tables I and II.[1]

Table I—Volume of solution, 200 cc; 3 grams wool; A = neutral bath; B = bath containing 2 cc $N/10$ HCl

Concentration methylene blue Percent	Methylene blue adsorbed A mg	Methylene blue adsorbed B mg
0.05	98	81.9
0.1	132	102.5
0.2	145	109.1
0.3	143	114.0
0.35	159	118.7
0.4	160	119.0

Table II—Volume of solution, 200 cc; 2 grams wool; C = bath containing 2 cc $N/10$ NaOH; D = bath containing 3 cc $N/10$ NaOH

Concentration methylene blue Percent	Methylene blue adsorbed C mg	Methylene blue adsorbed D mg
0.1	110	146
0.2	127	151
0.3	134	152
0.4	142	156

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[1] Pelet-Jolivet: "Die Theorie des Färbeprozesses," 117 (1910).

These tables show that less dye is taken up in the acid solution than in the neutral one and that somewhat more dye is taken up in the more alkaline than in the less alkaline solution. It is a pity that the two tables were not comparable so that we had a continuous series from the acid to the alkaline solution. The change from 3 to 2 grams of wool was made because "in presence of alkali, it was necessary to cut down the amount of wool in order to keep the dye from being completely adsorbed." This is a good and sufficient reason for not using 3 grams of wool in the alkaline solution but there is no apparent reason why 2 grams of wool could not have been used in the experiments with the neutral and the acid baths. Pelet-Jolivet tries to get round this difficulty by reducing everything to milligrams of dye per gram of wool, which gives him Table III.[1] This table shows exactly what I wish to bring out; but unfortunately the figures have no significance. If one plots concentration in solution against concentration in wool, one can change the units to suit oneself provided that the change be mentioned. If one is plotting initial concentrations against final concentrations in wool, it is not permissible to change the units. In Table III it is not true that 1 gram of wool will take up 44 mg of methylene blue from 200 cc of a one-tenth percent solution. It would really

TABLE III—Volume of solution, 200 cc; A = neutral bath; B = bath containing 2 cc $N/10$ HCl; C = bath containing 2 cc $N/10$ NaOH

Concentration methylene blue Percent	Methylene blue adsorbed, mg per g wool		
	B	A	C
0.05	27.3	33	49
0.1	34	44	55
0.2	36.7	48	63.5
0.3	38	48	66.9
0.35	39.5	53	—
0.4	39.6	53.1	71

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[1] Pelet-Jolivet: "Die Theorie des Färbeprozesses," 118 (1910).

take up more. The 44 mg is one-third what 3 grams of wool would take up, which is quite a different thing. Pelet-Jolivet's otherwise admirable work is not so effective as it should be, owing to his frequent failure to make comparable measurements.

Fortunately, there are other data which can be used. In one set of experiments Pelet-Jolivet[1] took 100 cc of 0.8 percent methylene blue solution. This was diluted to 200 cc and 3 grams of wool left in the flask for four days at 17°. When diluted with 90 cc water + 10 cc $N/10$ HCl, the wool adsorbed 22 mg methylene blue. When diluted with 100 cc water, 156 mg methylene blue were adsorbed. When diluted with 92 cc water + 8 cc $N/10$ NaOH there were 249 mg methylene blue adsorbed. Similar results were obtained with silk and cotton, Table IV.

TABLE IV—A = 0.3 gram silk in 50 cc 0.2 percent methylene blue; B = 3 grams cotton in 100 cc 0.1 percent methylene blue

Fibre	Methylene blue adsorbed, mg		
	2 cc $N/10$ HCl	Neutral solution	2 cc $N/10$ KOH
Silk (A)	1.3	10.8	40.6
Cotton (B)	1.2	11.2	30.0

The effect of a readily adsorbed anion is shown[2] in Table V. For the same concentration of acid, more dye is taken up

TABLE V—Volume of solution, 200 cc; 3 grams wool; 0.8 percent methylene blue

Acid added cc	Methylene blue adsorbed, mg		
	$N/10$ HCl	$N/10$ H_2SO_4	$N/10$ H_3PO_4
0	156	156	152
10	22	37	79
20	20	27	32
30	17	156	—

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[1] "Die Theorie des Färbeprozesses," 95 (1910).

[2] Pelet-Jolivet: "Die Theorie des Färbeprozesses," 95 (1910).

in a phosphate solution than in a sulphate solution while still less is adsorbed from a hydrochloric acid solution and we should expect the phosphate radical to be adsorbed the most and the chloride radical the least. This comparison is not strictly accurate because equivalent concentrations of two acids do not necessarily mean equal degrees of acidity. On the other hand, the amount of hydrogen as ion in 20 cc $N/10$ H_2SO_4 is unquestionably greater than in 10 cc $N/10$ HCl after both have been diluted to 200 cc, and, yet, more methylene blue is taken up in this sulphuric acid solution than in the hydrochloric acid solution. The difficulty in regard to the acidity can be got round by adding salts. Some data[1] are given in Table VI. At every concentration of dye more dye is fixed in the bath containing sulphate than in the bath containing no added salt, and there is still more dye adsorbed in the phosphate solution. We thus have $Na_2HPO_4 > Na_2SO_4 > NaCl > H_2O$. Just as should be the case, sodium sulphate increases the amount of a basic dye taken up, whereas it decreases the amount of an acid dye adsorbed. With 0.5 gram silk in 50 cc 0.2 percent methylene blue solution, the amounts of methylene blue taken up were 28.6, 18.4, 13.3 and 10.8 mg when sodium phosphate, sodium sulphate, sodium chloride, and nothing were added, respectively, to the solution.[2] With cotton there was no difference under the same circumstances; but there is a marked difference when the cotton

TABLE VI—Volume of solution, 100 cc; 1 gram wool

Methylene blue Percent	Methylene blue adsorbed, mg		
	No salt	0.06 Na_2SO_4	0.06 Na_2HPO_4
0.1	35	45.6	81.1
0.2	40	52.2	91.3
0.3	43	56.4	95.6
0.4	44	59.4	98.6

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[1] Pelet-Jolivet: "Die Theorie des Färbeprozesses," 118 (1910).

[2] Ibid., 98 (1910).

has been treated with tannin. The effect of different cations was also studied by Pelet-Jolivet who found that silk took up 13.3 mg methylene blue from a solution containing sodium chloride and only 6.3 mg from a solution containing barium chloride. With wool the depth of the color decreases in the following order: sodium phosphate, sodium sulphate, no addition, barium chloride, and platinum tetrachloride. Cotton takes up less methylene blue from a solution containing barium chloride than from one containing sodium chloride.

Pelet-Jolivet[1] sums up his experiments as follows: "From these experiments it is clear that the negative ions SO_4'' and PO_4''' have increased the dyeing power of methylene blue (a basic dye) while the positive ions $Ba^{\cdot\cdot}$ and $Pt^{\cdot\cdot\cdot\cdot}$ have decreased it. The ions of the electrolyte act on dyeing as they do on the precipitation of colloids, since they follow the valence rule (Schulze's law) . . . .

"The results may be summed up in the following rules:

Action of Acids and Bases

"*Acids (hydrogen ions) decrease the dyeing by the basic dyes and increase that by acid dyes. This action is proportional to the concentration of the hydrogen ions. Bases (hydroxyl ions) have just the opposite action.*

Action of Salts

"*Ions having the opposite charge from that of the dye facilitate dyeing; ions with the same charge check it. Multivalent ions have a stronger effect than univalent ones.*

"The first question that occurs to one is whether these rules hold in all cases. So far as the present investigations go, they do hold for acid and basic dyes, and we have made some experiments to test this. Of course it is necessary to keep in mind the physical and chemical actions which the electrolytes may have on special dyes because such factors are apt to interfere with the contact electrification. As an instance of this we may take potassium ferrocyanide (yellow

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[1] "Die Theorie des Färbeprozesses," 97, 99 (1910).

prussiate of potash, $K_4Fe(CN)_6$). The quadrivalent ferrocyanogen anion ought theoretically to increase the dyeing by basic dyes very much. If one adds this substance to the dyebath the dye is precipitated completely and consequently has no dyeing action. If, however, the fibers are mordanted beforehand with potassium ferrocyanide, the dyeing is stronger than with the other samples.

"Another case is that of fuchsine in presence of caustic soda. If wool is dyed in a hot bath, Vignon noticed that the fibers are scarcely colored so strongly as in the neutral and in the acid bath. This is due to the conversion of the fuchsine into a colorless base. If the wool is dyed in a cold bath under suitable conditions, the wool is dyed a deeper color in the presence of caustic soda than in the neutral or acid bath."

When discussing the general question of adsorption of a salt,[1] it was pointed out that a solution will become acid in presence of a substance which adsorbs the basic radical more readily than the acid radical. Silk has such a selective adsorption for rosaniline (magenta) that it will not only decompose the salt, leaving the acid behind, but it will convert the carbinol base back into the color base in presence of an excess of ammonia.[2] Another, though less striking experiment with silk and rosaniline has been carried out by Mills.[3] "At the heat of boiling water a solution of rosaniline hydrochloride or acetate undergoes more or less complete dissociation, attended, of course, by loss of color. Thus, for example, if a solution of either of those salts, containing 0.0000003 gram in 1 cc [three-tenths of a milligram per liter] be boiled for half an hour, complete decoloration ensues. But a piece of purified silk, immersed in the liquid, is almost immediately dyed red. We thus have the remarkable phenomenon, admirably suited to illustrate dissociation for a lecture, of silk being dyed red with a colorless solution of magenta."

One theoretical difficulty in regard to dyeing with basic

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[1] Bancroft: Jour. Phys. Chem., **18**, 5 (1914).

[2] Jacquemin: Comptes rendus, **82**, 261 (1876).

[3] Jour. Chem. Soc., **35**, 27 (1879).

colors is that, in many cases, the free color base is instable and that addition of alkali to a solution of rosaniline hydrochloride, for instance, gives rise to a colorless carbinol form. Since silk is dyed red from an ammoniacal solution of rosaniline, it has seemed to people that it must necessarily be present in the fiber as a salt. If the acid radical does not come from the solution, it must come from the silk and then we are back at the chemical theory of dyeing again. So important does this matter seem to the organic chemists that a prominent chemist once said to me that he would gladly accept my views on dyeing if it were not for the difficulty in regard to the basic dyes. It will therefore be desirable to discuss this point in some detail and I begin by quoting from a paper by Freundlich and Losev.[1]

"Qualitative experiments with a solution of crystal violet or of new fuchsine, which had been decolorized by blood charcoal, showed conclusively that the solution was distinctly acid to litmus paper and that it clouded on addition of silver nitrate.[2] Before determining the amount of chlorine ion quantitatively, it seemed advisable to purify the charcoal again thoroughly. The coarser particles were removed by sedimentation and thrown away. The charcoal was then boiled three times with concentrated hydrochloric acid and washed by decantation with boiling water until no test for chloride could be obtained. It was washed with conductivity water until Nessler's reagent gave no test for ammonia.

"This charcoal was now added to a crystal violet solution of known concentration, shaken, filtered, and washed. The filtrate was concentrated carefully in a platinum dish and the amount of chloride determined. It corresponded to 0.02701 gram hydrochloric acid while 0.4175 gram crystal violet should give 0.02758 gram hydrochloric acid. The charcoal was free

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[1] Zeit. phys. Chem., 59, 299 (1907).

[2] When evaporated with a few drops of Günzburg's reagent for free hydrochloric acid (more properly for hydrogen ion of a definite concentration) a red color developed, while this did not occur with water which had been shaken with pure charcoal.

from any ash that was soluble in acid; but it did contain a residue (5-8 percent) which was insoluble in acid and which was either silicic acid or silicate. The possible criticism, that the silicic acid was responsible for the separation of acid and base, would never be made by anybody who had seen the phenomenon. The adsorption of the crystal violet had changed the appearance of the charcoal quite uniformly and homogeneously in a way which will be discussed later. Since the hydrochloric acid was set free practically quantitatively, the color base must necessarily be distributed over the surface of the 95 percent charcoal (5 percent ash). Nevertheless the same experiment was tried repeatedly though qualitatively with a sugar charcoal (Kahlbaum) containing only 1 percent of insoluble impurity, always with the same result. Finally the best quality of gas soot was boiled three times with concentrated hydrochloric acid and then washed in the usual way until there was no test for chloride or for sulphate, a common impurity in soot. This purified soot gave no insoluble residue but it decolorized a crystal violet solution readily; the filtrate was acid and clouded with silver chloride when silver nitrate was added. The color of the dyed soot was the same as that of the blood charcoal.

"From these experiments it follows conclusively that markedly capillary substances such as charcoal and fibers make the basic dyes decompose into base and acid in such a way that the *acid remains in the solution while the base precipitates on the surface.* This raises two questions. Is the base present on the surface as such or in the form of a salt? With what other phenomena is this peculiar decomposition connected?

"That one must always speak of adsorption follows clearly from the observed form of the concentration function and from the other relations.

"In favor of the assumption of a salt formation we have as strongest arguments, the color of the dyed fibers and the previously mentioned fact that the fiber is dyed the same color from an alkaline solution of the dye. Something similar can also be noticed with the charcoal. Charcoal, which has been dyed with crystal violet, is of an absolutely uniform gold-brown color, somewhat duller than the crystals of the dye itself. When new fuchsine is used, the surface of the charcoal is greenish.[1] Charcoal has this same greenish appearance when it has taken up new fuchsine from an ammoniacal solution. The coloration can be seen very distinctly if one looks at the dyed charcoal in a thin-walled glass alongside of an undyed sample, using reflected light. The appearance of the same golden brown color, which solid crystal violet has, makes it probable that what is on the charcoal is also violet by transmitted light; merely the depth and uniformity of the layer cause the predominance of the surface color. One can therefore say that with charcoal as with the fiber the color is what one would expect if the dye were present as salt.

"On the other hand, the hypothetical compound of charcoal as acid and the crystal violet base does not behave at all as one would expect it to do. That it is formed in a few seconds from two substances having high molecular weights, is perhaps less improbable than it at first seems to be, for many molecular compounds of substances having high molecular weights are formed practically instantaneously (many picric acid compounds, for instance). It is very improbable, however, that such a compound should not be hydrolyzed by water; most of the picrates break down readily when washed with water. If one decolorizes a crystal violet solution completely by means of charcoal, then filters and washes the charcoal, the dyed charcoal is not changed in any way by water. One can shake a small or a large amount of the dyed charcoal without the water becoming colored to the slightest extent even after weeks, in spite of the fact that crystal violet has so great a coloring power that 0.15 mg (0.00000037 mol) per

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[1] Lehmann (Zeit. phys. Chem., 14, 157 (1893)) noticed a bronzed effect on India ink which had adsorbed dyes. A similar coloring of colloidal gold after sedimentation in a fuchsine solution has been noticed for instance by Zsigmondy (Zur Erkenntnis der Kolloide: Jena, 1906).

liter can be detected in a 10 cm layer. Charcoal dyed with fuchsine behaves in the same way.

"The question now arises how these experiments can be reconciled with the previously described ones on equilibrium. There it was found that the same concentration was reached when a concentrated solution was adsorbed and then diluted as when the adsorption took place with the same amount of solution at the final dilution. Since more substance is usually adsorbed from a concentrated solution than from a dilute solution, the charcoal should lose dye when the solution is diluted, and yet, according to these last experiments, the dyed charcoal lost no dye to the water.

"This apparent contradiction disappears when we recall that we were diluting an acid solution in the equilibrium experiments, and that the adsorbed dye is extracted in an acid solution but not in pure water. It is worth stating that this apparent discrepancy occurs only with the basic dyes. There is no decomposition with the acid dyes (patent blue, crystal ponceau) and the adsorbed dye is extracted somewhat by water. The equilibrium experiments hold here without limitation."

This explanation is given up in a later paper[1] in which the authors say: "Subsequent experiments showed, however, that this explanation would not do. Very concentrated acid solutions are necessary in order to extract visible amounts of dye from charcoal dyed in the way described; very dilute acid solutions, such as occur in the equilibrium experiments, behave like pure water.[2]

"As a matter of fact there is no discrepancy at all, a fact which was noticed by one of us (Neumann). It is a necessary consequence of the existence of an adsorption equilibrium

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[1] Freundlich and Neumann: Zeit. phys. Chem., 67, 539 (1909).

[2] To a certain extent the case is different with crystal violet because the exponent $1/n$ in the adsorption isotherm $x/m = \alpha . c^{1/n}$ is so near zero that the adsorbed amount is practically independent of the equilibrium concentration and the equilibrium experiments therefore lose their significance. What has been said holds, however, for new fuchsine and brilliant green.

that a dyed charcoal, which is in equilibrium with a completely decolorized solution, will give up to pure water an amount of color which is not sufficient to color the water. The equilibrium concentration with freshly added pure water must be somewhat less than that of the dye solution which had been shaken with charcoal. If the color in the latter solution is below the limit of visibility, this must be still more true for the pure water.

"Such a misconception of the equilibrium relation, as occurred in the other paper, can be excused only by the fact that the appearances were very misleading. Charcoal, dyed with crystal violet or brilliant green as a result of decolorizing a concentrated dye solution, has the same golden luster as the crystals of the dye, and one involuntarily compares the two and is astonished that no dye dissolves from the charcoal whereas the crystals color water at once. One forgets that the dyed charcoal was in equilibrium with a decolorized solution.[1]

"It was scarcely necessary to test the accuracy of this point of view because the equilibrium experiments of Freundlich and Losev were sufficient. Merely as an illustration the following experiments were made: Charcoal was dyed once in a brilliant green solution so that the solution was exhausted. In a second experiment the amount of charcoal was so regulated that the solution was still moderately colored. Both solutions were filtered from the charcoal as completely as possible. When the first sample of charcoal was treated with water, the wash water was colorless; in the case of the second sample the liquid was green even when relatively large amounts of wash water were taken.

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[1] In the literature are to be found a number of experiments intended to test the question of an adsorption equilibrium, which were arranged so unsuitably that the solution was exhausted. When the adsorbing material was shaken with water and practically none of the adsorbed substance dissolved, people made the mistake of doubting the occurrence of an equilibrium. In such experiments the concentration in the solution after adsorption must be measurable.

"From a proper consideration of adsorption equilibrium it follows that a dye can be fast without having to assume a special combination between fiber and dye. It is only necessary that the exhaustion of the dye-bath shall be so complete that it is not colored visibly. The concentration of the dye in the wash water will be smaller still and the dyed fibers will never bleed."

After this digression we can come back to the Freundlich and Losev[1] paper.

"If one rejects the rather improbable assumption of a salt-like compound between charcoal and color base, there is nothing else to assume but that the color base occurs in the charcoal surface either as such[2] or as a derivative of the same."

"As a matter of fact the substance adsorbed by the charcoal behaves quite differently from crystal violet as salt. While water will not dissolve anything from the dyed charcoal, the dye is extracted without difficulty by other solvents. Methyl and ethyl alcohol become colored deep violet in contact with the dyed charcoal, and so do amyl alcohol (somewhat redder) and pyridine. The adsorbed substance is also much more soluble in benzene than the crystal violet salt. If one shakes crystal violet with anhydrous benzene, the liquid does assume a bluish violet tinge; but this is due to suspended particles, for the benzene filters practically colorless through as ash-free paper filter and a strip of filter paper, dipped into the filtrate, dries to an extremely faint bluish color. If one shakes benzene with a large amount of charcoal, which has been dyed with crystal violet, the benzene becomes colored yellowish brown. If one dips a piece of filter paper into

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[1] Zeit. phys. Chem., 59, 300 (1907).

[2] In a later paper (Freundlich and Neumann: Zeit. phys. Chem., 67, 548 (1909)) this is modified to read: "The substance, which is present on the charcoal surface after the adsorption of the dye, is in all probability a salt of the color cation with a strongly adsorbed, presumably organic, anion. Of course it is not impossible that the anion is the strongly adsorbed hydroxyl ion and that the color base is adsorbed, but this is not a necessary conclusion."

this solution, the paper takes on a deep blue-violet color, and the benzene solution becomes the same color if alcohol be added to it.

"Attention has already been drawn to the fact that acids also extract dye from the charcoal. New fuchsine behaves similarly to crystal violet in all the points under consideration though the solutions of new fuchsine have not been studied with so much care.

"We are now face to face with the question as to the form in which the base occurs on the charcoal surface. Before answering this question we must consider more carefully the chemical properties of the bases of the color salts in question. Differences of opinion as to these color bases have persisted even up to the most recent times. The reason for this is to be found in the rather obscure isomeric relations. The color salt of crystal violet behaves exactly like the salt of a strong base. It is highly dissociated[1] and a basic carbonate is known.

"One would therefore expect a highly dissociated hydroxide to exist, having the same color as the salt and soluble in water, by analogy with the strong alkalies. This hydroxide does not exist as a base which can be precipitated. If one adds caustic potash, for instance, to a solution of crystal violet, the solution becomes decolorized and clouded; there separates a white precipitate, the carbinol, which has the composition of the desired hydroxide but none of the required properties. It is only sparingly soluble in water, does not conduct appreciably, and is not colored.

"By conductivity measurements on a solution containing crystal violet and one equivalent of NaOH, Hantzsch[2] showed that the conductance of the solution was what it would be in case the solution contained a mixture of dye cation + $Na^{\cdot}$ + OH' + Cl', thereby proving the possible existence of the 'true' base in aqueous solution. In course of time the con-

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[1] Hantzsch: Ber. chem. Ges. Berlin, 33, 278 (1900).

[2] Ber. chem. Ges. Berlin, 33, 278 (1900); Miolati: Ibid., 26, 1788 (1893); 28, 1696 (1905).

ductance of the solution decreased markedly, finally reaching the value for NaCl, while at the same time carbinol precipitated. Therefore there takes place the reaction

$$\text{dye cation} + OH' = \text{carbinol}.$$

The fact that the rate of formation of the carbinol is proportional to the first power of the concentration of dye and of hydroxyl ion is additional evidence of the correctness of this point of view. A welcome confirmation and extension is to be found in the recent work of Sidgwick and Moore.[1] They followed colorimetrically the action of alkali in converting brilliant green into the colorless carbinol. With this dye, which is closely related to crystal violet, they found the same relation in regard to concentration of the dye and of hydroxyl ion which Hantzsch had found; and the constants also had the same value as those determined electrically. Hantzsch was therefore correct in ascribing this group of reactions to those phenomena of isomerism which he calls the isomerism of the pseudo-acids and pseudo-bases. He considers the 'true' base as ammonium base while the carbinol is the pseudo-base.

"Baeyer[2] considers an isomerism, ammonium base—carbinol, as improbable and prefers to speak of an isomerism, carbonium base—carbinol.

"As far as the present question is concerned, it is a matter of indifference what type of isomerism we have. It is only important whether the colored base can be isolated. This appears not to be the case. A discussion of this matter by von Georgievics and Weil[3] led to no definite conclusion whether the colored precipitates, which are obtained by a suitable addition of alkali to the solution of the dye, are or are not mixtures of the dye salt and carbinol. Hantzsch observed the ammonium base only in aqueous solution and Baeyer

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[1] Zeit. phys. Chem., **58**, 385 (1906).

[2] Ber. chem. Ges. Berlin, **37**, 1183, 2848 (1904); **38**, 569 (1905).

[3] von Georgievics: Mitt. Gew. Museum, 1894; Ber chem. Ges. Berlin, **29**, 2015 (1896); Monatshefte für Chemie, **17**, 4 (1896); **21**, 40 (1900). Weil: Ber. chem. Ges. Berlin, **28**, 205 (1895); **29**, 1541, 2677 (1896); **33**, 3141 (1900).

is of the opinion that the color bases have a definite but very limited stability.

"One cannot, therefore, consider it probable that the ammonium base is present on the charcoal surface. There is also another argument against such a conception, namely that the substance in question is so insoluble in water.[1] The ammonium base ought to be soluble in water by analogy because it is a strong base, and also because the addition of alkali to a solution of crystal violet does not at first change the color at all. Since nothing precipitates, the ions of the color base must co-exist with hydroxyl ions, though of course it might be urged that there was supersaturation.

"We also cannot assume the presence of carbinol on the charcoal surface. This assumption is contradicted by the color of the adsorbed substance, which is a lustrous golden brown in the case of crystal violet, not unlike the color of the dye salt. The hypothesis that one is dealing with a mixture of carbinol and dye salt seems scarcely to be a happy one in view of the previously described properties of the adsorbed dye.

"The properties of the substance adsorbed on the surface of the charcoal correspond therefore neither to those of the ammonium base nor to those of the carbinol. The important properties are as follows:

1. The substance must be formed by splitting off acid from the dye salt.
2. It has a golden brown surface color in the case of crystal violet and probably a violet body color.
3. It is insoluble in water [when in contact with charcoal].
4. It is soluble in alcohol, pyridine, etc., with violet color.
5. It is soluble in benzene with reddish brown color.

"It occurred to us that the polymerization products of fuchsonimine as described by Baeyer, corresponded sur-

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[1] [This argument has been recognized specifically as unsound. Freundlich and Neumann: Zeit. phys. Chem., 67, 540 (1909).]

prisingly with the observed properties of the substance adsorbed on the charcoal surface. These products were obtained by grinding parafuchsine very fine in a mortar, treating with concentrated caustic soda, filtering, washing with water, and drying in a vacuum. There was obtained a brown amorphous powder which contained only traces of chlorine and which, on analysis, proved to have practically the composition of the carbinol. It was completely insoluble in water but soluble in alcohol and in pyridine.

"Now Baeyer considers this compound as a condensation product of the imine compound $(NH_2C_6H_4)_2C.C_6H_4.NH$, and there is no justification for such a compound in the case of a peralkylized substance like crystal violet. On the other hand, the similarity in the behavior of the two substances, crystal violet and fuchsine, is so great that it does not seem impossible that similar polymerization products may be formed under similar conditions.

"This is actually the case. Finely powdered crystal violet was ground with caustic soda. It changed into a brownish violet amorphous powder which was sparingly soluble in water.[1] It was collected on a filter and washed, whereby it appeared that the caustic soda and the wash water had removed quantitatively all the chlorine contained in the dye. As soon as the wash water gave no further test for chloride, the powder was dried in a vacuum. It dissolved in alcohol and pyridine with a violet color and in benzene with a reddish brown color. When a piece of filter paper was dipped into the benzene solution and then allowed to dry, it became colored a deep violet. If alcohol were added to the benzene solution, a change to violet occurred. It is strikingly evident that the properties of this substance resemble very closely those of the substance adsorbed on the charcoal surface; loss of hydrochloric acid, color of the substance itself,[2] solubility relations, and color of the solutions."

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[1] We could not tell whether the slight color in the wash water was due to the new substance or to some unchanged dye salt.

[2] The color was not quite so brownish as that of the substance itself.

"The similarity with the behavior of fuchsine, and the ease with which the color salt can be regained by the action of acids, forces the conclusion that one is dealing with a condensation product of the carbinol or, more properly speaking, of the carbonium hydroxide or of the ammonium base. Unfortunately, external conditions prevented for the moment the quantitative study of these results. We have not yet determined how long these substances will keep and whether they change in time to carbinol in presence of hydroxyl ion. As the result of the latest experiments and considerations we may say that *charcoal splits the dye salt into base and acid, and that the base is very probably present on the charcoal surface as a condensation product of the true active colored base.*

"It should be mentioned that this conception fits in admirably in other respects with other facts. From the description of these substances, it appears that they are amorphous and colloidal. Amorphous substances are readily compressible, and compressible substances are adsorbed strongly, by surfaces or their formation is favored by surfaces. That is also the case here and we are justified in considering the union between charcoal and the condensation products of the color base as a stable colloid complex of a positive colloid (color base) and a negative colloid (charcoal), like those made familiar by the work of Zsigmondy, Biltz[1] and others.

"The question now arises as to the relation between the fibers and the dyes. Since there is an unbroken analogy between the behavior of charcoal and that of fibers, we are forced to conclude that a similar product of the color base is adsorbed by the fibers and a similar colloidal complex formed. Here it may be mentioned that wool dyed with crystal violet is not decolorized by water but is by alcohol. In the literature there are numberless statements that the last traces of dye cannot be removed by alcohol but our experiments do not confirm this. The decolorized wool was just as

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[1] Ber. chem. Ges. Berlin, 37, 1096 (1904).

yellowish white as the wool which had never been dyed. Sisley[1] also states that silk, which has been dyed with fuchsine, can be decolorized completely. He was able to repeat the cycle several times *without the silk losing in weight at all*, a further, and decisive, proof against the assumption of a salt formation between dye and fiber. It was unfortunately not possible to carry out an experiment on the removal of the dye from the fiber by means of benzene because the somewhat swollen fibers were uncommonly difficult to wet with benzene.[2] The difference in coloration between fiber and charcoal is not important; with the orderly arrangement on the charcoal surface, the surface color is the predominant one. With the fibers there is no such even distribution on the surface of an opaque substance, and consequently the body color is the important one. It is however well known among technical men that in certain cases (with concentrated dyebaths for instance) the fibers are dyed so deep a shade that the precipitated dye gives rise to a bronze effect similar to that on charcoal. The surface bronzing thus depends only on the amount of adsorbed dye and it shows up at lower concentrations with charcoal owing to the relatively smaller surface and greater adsorption.

"This is the place to describe a peculiar phenomenon which has been noticed with deeply dyed carbon. If one adds a layer of benzene or any other organic solvent such as chloroform, anisol, aniline or nitrobenzene (carbon bisulphide and ligroin scarcely act at all) to water in which is suspended charcoal dyed with crystal violet and in which there is not the slightest trace of color there appears in the course of time, say ten minutes, a violet edging at the surface between water and benzene (or the other solvents) which gradually spreads more and more into the water until the water is colored a deep violet. This color is permanent so long as there is a layer of benzene above the water. As soon as all the benzene has evaporated

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[1] Bull. Soc. chim. Paris, 25, 865 (1900).

[2] [It seems quite possible that this is the explanation for Walker and Appleyard's unexpected results with silk, picric acid, and benzene.—W. D. B.]

the dye is all taken up again by the charcoal and the water becomes colorless again. If another layer of benzene is added to the water, the cycle repeats itself. In some cases this is done four or five times without any noticeable variation. A few grans of dyed charcoal are sufficient for the experiment.

"The phenomenon is probably due to the fact that the base, or the condensation product, adsorbed by the charcoal is more soluble in organic solvents than in water; also, according to the experiments of Freundlich,[1] adsorption is much less in organic solvents than in water.[2] The adsorbed substance dissolves more readily in the benzene or in the water saturated with benzene; and since it is less adsorbed, a certain amount will pass into the liquid. One might be surprised that the small amount of dissolved benzene could change the properties of the water so much; but this is actually the case. If one shakes benzene with water, gives the two layers plenty of time to separate, and draws off the water by means of a separatory funnel into a glass in which charcoal, dyed with crystal violet, is suspended in water, the liquid colored becomes uniformly violet. This experiment can only be interpreted to mean that the adsorbed base is more soluble and less adsorbed in water containing benzene. The violet color seems strange at first because it has already been mentioned that the base, adsorbed by the charcoal, dissolves in benzene to form a brown solution. If one remembers that addition of alcohol causes this color to change to violet, the violet color of the aqueous benzene solution ceases to be extraordinary.[3] New fuchsine and brilliant green behave exactly like crystal violet; exceptionally good results are obtained when ether is substituted for benzene."

Before discussing Freundlich's conclusion that we are dealing with a condensation product, it will be desirable to

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[1] Zeit. phys. Chem., 57, 385 (1906).

[2] [This is true only in so far as it is a restatement of the greater solubility in organic solvents.—W. D. B.]

[3] For the existence of similar, colored, dye bases in organic solvents, see Michaelis: Pflüger's Arch., 97, 634 (1903); 101, 183 (1904).

see exactly what Baeyer and Hantzsch say in regard to the existence of ammonium bases. I quote first from a paper by Baeyer and Villiger.[1]

"Hantzsch[2] has studied the conductance of the system, dye salt + NaOH, and has drawn the conclusion that the real color bases have the formula of an ammonium hydroxide. He has expressed this opinion so forcibly that these ammonium hydroxides are even to be found given in text-books as real compounds. We will now describe a few experiments which show that Hantzsch's experiments do not constitute a convincing proof of the existence of the ammonium hydroxides.

"As regards the behavior of fuchsine and new fuchsine with alkalies, Homolka has shown that ether, benzene, or chloroform extracts the brownish orange, quinoid base from the alkaline solution. This base is readily soluble in water and consequently is partially removed from the organic solvents by water. This accounts for the fact that a concentrated solution in ether is obtained when an excess of caustic soda is added so as to salt out the base. If one adds a solution of Homolka's base—preferably from new fuchsine in benzene—to a dilute sodium chloride or potassium nitrate solution, a precipitate is obtained which contains a large amount of fuchsine. The quinoid color base has therefore taken hydrochloric acid from the caustic soda and has set free caustic soda as may be shown by testing with turmeric paper.[3] If the benzene solution is dilute and the sodium chloride is likewise very dilute, say $N/100$, there is no appreciable precipitation and the aqueous solution has a color intermediate between that of fuchsine and that of the imine base. From this one must conclude that fuchsine is present in the solution even though the dilution is so great that none precipitates. Consequently there must be present simultaneously in such a

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[1] Ber. chem. Ges. Berlin, 37, 2858 (1904).

[2] Ibid., 33, 258, 752 (1900).

[3] Weil has previously shown that fuchsine carbonate and sodium chloride react to form fuchsine and sodium carbonate, as can be shown by the alkaline reaction of the solution.

solution, imine base, fuchsine, sodium chloride, sodium hydroxide, and carbinol. We can also show that imine is formed when one equivalent or less of caustic soda is added to a fuschine solution because ether is colored brown when shaken with the alkaline solution.

" If we keep these facts in mind when testing the accuracy of Hantzsch's conclusion, we see that the existence in solution of a colored ammonium hydroxide is by no means proved. In the first place it is not correct to say[1] that ether extracts no imine base from a solution containing fuchsine and one equivalent of caustic soda. The ether becomes distinctly brown and the carbonate is formed if one passes carbon dioxide through the ethereal solution. That the ether contains only a little imine base is not because very little of the fuchsine has been decomposed but because the imine is readily soluble in water. If one salts out the imine base by an excess of caustic soda, the ether of course takes up more of it.

"In the second place, Hantzsch has calculated the conductance on the assumption that the system, fuchsine + 1 NaOH, changes at once to the system, fuchsine ammonium hydroxide + NaCl, which then reacts in two different ways, to form imine base + NaCl, and carbinol + NaCl. This assumption is inaccurate for two reasons.

"Let us adopt Hantzsch's point of view and assume that fuchsine is the salt of an ammonium hydroxide having the same strength as caustic potash. In the system, fuchsine + 1 NaOH, we shall then have an equilibrium between fuchsine, ammonium hydroxide base, sodium chloride and caustic soda. The observed conductance will therefore not be due solely to the ammonium hydroxide base but also to the sodium hydroxide. If, however, we adopt our assumption that fuchsine reacts with NaOH to form NaCl and imine base, which latter reacts with sodium chloride to form fuchsine again, the composition of the solution will be given by the equation

fuchsine + 1NaOH = fuchsine base + imine base + NaCl + NaOH

and one would naturally expect an increase in conductance due

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[1] Hantzsch: Ber. chem. Ges. Berlin, 33, 759 (1900).

to the presence of sodium hydroxide. The conductance will finally decrease to that of a sodium chloride solution owing to the imine base taking up water and forming carbinol. According to this way of looking at things, there is no change of an ammonium hydroxide into a pseudo-base but rather an addition of water by a quinoid substance.

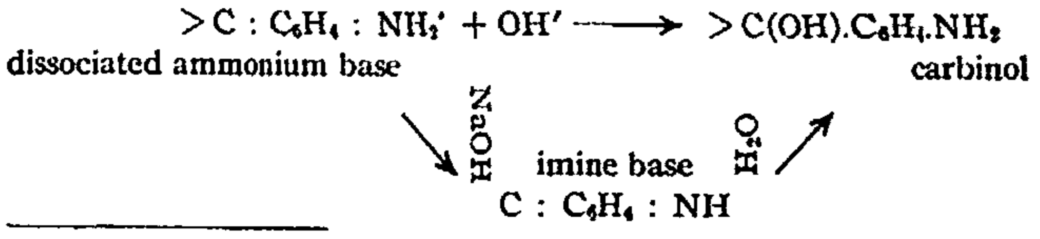
"With the completely alkylated dyes, such as hexamethyl violet [crystal violet] we may assume, with Hantzsch, that the true color base is an ammonium hydroxide. If this base could be isolated, it would behave towards sodium chloride like the imine base of fuchsine and we therefore believe that what has just been said holds also for hexamethyl violet and that the large and gradually decreasing conductance, which Hantzsch found for hexamethyl violet + 1 NaOH, is due to the conductance of the caustic soda, the amount of which decreases owing to formation of carbinol. We base this conclusion upon the action of an excess of alkali in decolorizing rapidly a solution of crystal violet. This seems to us to prove that the hypothetical ammonium hydroxide base can exist only for an immeasurably short time. It might be objected that the rapid conversion of the ammonium base to pseudo-base by the excess of caustic soda is due to the salting-out action of the latter; but this objection falls to the ground in view of the fact that ammonia decolorizes the solution of hexamethyl violet almost as rapidly as caustic soda and yet does not salt out at all. According to Hantzsch hexamethyl violet is the salt of a base as strong as caustic potash and consequently it should either not be decomposed at all by ammonia or only to a negligible extent. If the ammonium hydroxide base were also moderately stable, one does not see why a crystal violet solution should be completely decomposed by ammonia in a very short time—within a minute under some conditions.

"We therefore conclude that the true color base of fuchsine is not the ammonium hydroxide but Homolka's imine base, whereas the ammonium hydroxide is the true color base in the case of hexamethyl violet and all the completely alkylized dye salts, but is so instable that it cannot be characterized as capable of existence in a chemical sense. According to this point of view the conversion of an ammonium base into a pseudo-base occurs only in the case of the completely alkylized dye salts."

This criticism was not long left unanswered by Hantzsch.[1]

"In the latest paper on 'Dibenzalacetone and Triphenylmethane,' A. v. Baeyer and V. Villiger[2] have subjected my experiments and conclusions on the nature of the bases of the aniline dyes[3] to a criticism which unfortunately I cannot leave unanswered. Although, or more properly because, my results are convincing from the standpoint of the dissociation theory, the reputation and influence of the first of the two authors make it necessary for me to discuss in detail the objections to my conclusions.

"From my experiments on the conductance of the system, dye salt (RN.Cl) + sodium hydroxide, I concluded that, since the observed conductance is at first (almost) exactly equal to the sum of the conductance due to the four ions, $RN^{\cdot} + Cl' + Na^{\cdot} + OH'$, such solutions—of crystal violet and sodium hydroxide, for instance—contain the dye at first (almost) completely as the true ammonium base which, like the tetramethyl ammonium hydroxide, has almost the strength (degree of dissociation) of the alkalies. The ammonium bases of the dyes, however, are only temporarily stable even in the dissociated form, as shown by the gradually decreasing conductance of the aqueous solutions; they undergo isomeric changes, more or less rapidly into the pseudo-ammonium bases, the carbinols. There is a previous loss of water and change to an imine base in the case of those ammonium bases like fuchsine which still have hydrogen atoms attached to nitrogen.



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[1] Ber. chem. Ges. Berlin, 37, 3434 (1904).

[2] Ibid., 37, 2848 (1904).

[3] Ibid., 33, 278, 752 (1900).

"According to von Baeyer and Villiger my 'experiments do not constitute a convincing proof of the existence of the ammonium hydroxide;' the authors come finally to the conclusion that 'the true color base of fuchsine is not the ammonium hydroxide but Homolka's imine base, whereas the ammonium hydroxide is the true color base in the case of hexamethyl violet and all the completely alkylized dye salts, but is so instable that it cannot be characterized as capable of existence in a chemical sense.'

"Let me first point out that, according to the general custom due to the dissociation theory, we only consider strictly as bases the hydroxyl compounds, R.OH, which are more or less completely dissociated in aqueous solution into $R^{\cdot}$ and OH', in other words which furnish hydroxyl ions. We can only speak of ammonia as the base of ammonium chloride in the sense that we speak of carbon dioxide as carbonic acid. It is more importantto note however that although the true base of ammonium chloride, ammonium hydroxide, is not known in a free state and cannot be isolated, yet it is capable of existing chemically in the form of an ion, for the degree of dissociation of aqueous ammonia solutions as calculated from the conductance corresponds in fact to the amount of dissociated ammonium hydroxide. When these generally accepted methods of reasoning are applied to the present case, we see that the true color bases are the ammonium bases, that the imine bases are the anhydrides of the ammonia type, and that the amount of the dissociated ammonium bases in aqueous solution can be determined from the conductance just as in the case of ammonium hydroxide. This cannot easily be determined directly because of the isomeric change of the ammonium hydroxide to carbinols. It is therefore determined indirectly as before pointed out. Objection has been made by von Baeyer and Villiger to the reliability of this indirect method not only in the case of fuchsine but also in the case of the completely alkylized dyes, such as hexamethyl violet, which cannot form anhydrides of the ammonia type. According to their view one may assume that the true color base of hexamethyl violet is an ammonium hydroxide; but it is still to be proved that the hypothetical ammonium hydroxide base can exist even for an immeasurably short time.

"Since my conclusions from my experiments are quite different, I must give the course of reasoning at some length. If one had a pure aqueous solution of the crystal violet base and could show that it was practically completely dissociated, that would be in itself sufficient proof that the solution contained the ammonium base of crystal violet. Unfortunately this simple state of things can only be attained with difficulty and without accuracy owing to the rapid isomeric changes of the base. Instead of trying to do this, I have started with very highly diluted, and therefore practically completely dissociated, solutions of the dye salt and have added equally dilute, equimolecular solutions of caustic soda. The conductance of the mixture proved to be the sum of the conductances of the components. Consequently the system must contain the four coexisting ions, RN,[1] Cl, Na and OH.

"We can therefore attribute to a misunderstanding the statement of von Baeyer that I made the assumption that the system, dye salt + NaOH, changed at once into the system, ammonium hydroxide base of the dye and sodium chloride. The misunderstanding is probably due to the fact that the conductance of sodium chloride ($Na^{\cdot} + Cl'$) has to be substracted in order to obtain the conductance of the ammonium base ($RN^{\cdot} + OH'$). This process, though also criticized, is completely justified by the dissociation theory. . . .

"A dilute solution of crystal violet and caustic soda at first contains all four ions simultaneously. After deducting the conductance due to sodium chloride solution of that concentration, we get a conductance which is what we should expect if we had the dye cations and the hydroxyl anions coexisting at almost the same concentration that we should have with an equimolecular caustic soda solution at the same

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[1] Abbreviation for the cation of the color base.

dilution. From the dissociation theory we may conclude that the true hexamethyl violet ammonium base exists in these solutions and that it is almost as strong (dissociated) a base as the alkalies. Its instability in the undissociated 'free' state has nothing to do with the proved existence in the dissociated state. Nobody would question the existence of dissociated ammonium hydroxide in aqueous ammonia because it is impossible to isolate ammonium hydroxide. Solutions of the hexamethyl violet ammonium base change but slowly to the carbinol form, as is shown by the fact that the conductance of the solution goes back very gradually to that of the corresponding sodium chloride solution. Consequently von Baeyer and Villiger are not justified in saying that the hexamethyl violet ammonium base can exist only for an immeasurably short time.

"Equally erroneous are the experiments and reasoning which purport to show that I was not justified in assuming the existence of the fuchsine ammonium base. It is immaterial whether the conductance in the system, fuchsine salt + NaOH, is due in part to the caustic soda. The important fact is that at first (before the change to carbinol) large amounts of fuchsinium ions and hydroxyl ions there coexist unaltered, without there being an immediate change such as occurs with an aniline salt and caustic soda

$$\begin{aligned} \mathrm{ArNH_3Cl} + \mathrm{NaOH} &= (\mathrm{ArNH_3^{\cdot}} + \mathrm{Cl'} + \mathrm{Na^{\cdot}} + \mathrm{OH'}) \\ &= \mathrm{ArNH_2.H_2O} + \mathrm{Na^{\cdot}} + \mathrm{Cl'}, \end{aligned}$$

to the amine or to the imine base. That such solutions contain chiefly fuchsine hydroxide and only relatively small amounts of the imine base follows also from the color of the solutions according to Ostwald's views on the color of the ions. At 0° freshly prepared solutions of fuchsine salt + caustic soda have almost exactly the same color and intensity as equally highly diluted solutions of fuchsine salt without caustic soda. There are therefore practically equal amounts of the colored fuchsinium cations in the two solutions.

"It is possible to account for the behavior of Homolka's imine base only by considering its relation to the true dissociated ammonium color base. The imine base is not removed from solutions in ether, benzol, or chloroform very thoroughly by water because it is very soluble in water, since so complex a triphenyl methane base would dissolve but slightly in water. What happens is that the imine base is simultaneously hydratized and ionized by contact with water (like NH_3); and the new compound is readily soluble in water. What we have dissolved in the aqueous solution is not the imine but almost entirely the dissociated ammonium hydroxide. The brown base dissolves in indifferent solvents with a brown color; but anybody can see that in water we have a pure red solution of almost the same intensity as an equally concentrated fuchsine solution would be. Special experiments showed that the conductance of such solutions is almost as large as it should be for a completely dissociated ammonium hydroxide solution if we take into account the numerous and unavoidable experimental errors such as the rapid change of the fuchsine ammonium base to the carbinol, and the changes in conductance due to the varying amounts of ether or benzene, and also carbon dioxide, which are taken up when shaking out with water. Solutions of new fuchsine in benzene precipitate solid fuchsine when mixed under proper conditions with sodium chloride or potassium nitrate solutions; but this is not, as von Baeyer assumes, because the quinoid color base (imine base) has taken hydrochloric acid from sodium chloride, setting caustic soda free. In reality, the ions of the dissociated ammonium base have done this as soon as the concentrations exceeded the solubility product of the corresponding fuchsine salt. It is now possible to explain von Baeyer and Villiger's results that the brown imine base is extracted freely by indifferent solvents from an aqueous solution of fuchsine and sodium hydroxide. The aqueous solution contains chiefly the ions of the true ammonium hydroxide; there are also present small amounts of the imine base, just as in the case of aqueous solutions of all amines. Since the fuchsine imine base is readily soluble in ether and sparingly soluble in water, the ether removes practically all of the small amounts of imine base. The equilibrium is destroyed; more imine base is formed, which is then extracted by the ether, and so on.

"Strictly speaking, the action of caustic soda on solutions of dissociated fuchsinium hydroxide is not a salting-out but depends on a specific action of the hydroxyl ions which the mass law shows to be important in aqueous solutions of all ammonia derivatives.[1] In such systems as

$$R{:}N,\ H.OH \rightleftharpoons R.NH.OH \rightleftharpoons R.NH^{\cdot} + OH',$$

addition of caustic increases the concentrations of hydroxyl ions and, in consequence, the concentration of the undissociated portion. The shaking-out of the imine will therefore be aided and also the change to the pseudo-carbinol base accelerated. The following experiments show that caustic does not salt out such dye solutions at all but acts solely as a base by changing the concentration of hydroxyl ions.

"Very dilute solutions (*N*/200) of fuchsine and of crystal violet were decomposed simultaneously by equal volumes of

1. One molecular weight of caustic soda.
2. One molecular weight of ammonia.
3. One molecular weight of sodium chloride.
4. Pure water.

These solutions had at first the same intense red color, but the one containing caustic soda decolorized the most rapidly through precipitation of the carbinol bases. The solution containing ammonia changed more slowly and the one containing sodium chloride changed scarcely faster than the water one. Equal volumes of ether extract the most imine base from solution No. 1 and the least from solutions Nos. 3 and 4, which is exactly what one would expect according to the dissociation theory. These experiments show that the true ammonium color bases exist in the dissociated state for easily determined periods and not for immeasurably short times. They also show that ammonia does not decolorize

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[1] Cf. Hantzsch and Sebaldt: Zeit. phys. Chem., 30, 258 (1899).

a solution of hexamethyl violet practically as rapidly as does caustic soda; and lastly that excess of sodium hydroxide causes the rapid change of ammonium base into pseudo-base, not, as von Baeyer and Villiger assumed, because of a salting-out action but because of the hydroxyl ions, the rate of isomeric change being proportional to the concentration of the hydroxyl ions.

"I think that the results of my former experiments may now be considered as completely established. They may be summed up briefly as follows: The primary and actual bases of the dye salts of the triphenyl methane series are true ammonium hydroxides having the same color as the dye salts. They cannot be isolated in the 'free' (solid) state. They exist only in dilute aqueous solutions and therefore in a state of almost complete dissociation; their presence, however, can be shown just as definitely as that of dissociated ammonium hydroxide in aqueous ammonia solutions. They undergo isomeric change to the pseudo-bases or carbinol with a varying but always measurable velocity, the change being autocatalytic because proportional to the concentration of hydroxyl ions. The rate is therefore increased somewhat by ammonia and still more by sodium hydroxide. From aqueous solutions of bases like fuchsine which still contain a hydrogen atom attached to nitrogen, indifferent solvents extract anhydrides of another color (Homolka's brown imine base from fuchsine). This stands in exactly the same relation to the primary ammonium color bases as ammonia to ammonium hydroxide; the imine base is therefore not the true base but is the anhydride of that base and is converted by water almost completely to the dissociated ammonium base."

This reply by Hantzsch covers the ground very thoroughly, and in a later paper Baeyer[1] concedes practically every point of importance raised by Hantzsch. Baeyer prefers to consider the free base as a carbonium base instead of an ammonium base; but that is immaterial so far as the theory of dyeing is concerned.

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[1] Ber. chem. Ges. Berlin, 38, 580 (1906).

We can now consider the question as to the form in which fuchsine is taken up by the fiber from a colorless ammoniacal solution. Freundlich postulated the presence of condensation products of the imine base; but this was because he thought that the substance must be insoluble in water. As soon as he saw the error of this assumption, he also recognized that the color might be due to the ammonium base. The difficulty here is the alleged instability of the ammonium base; but I am inclined to think that this is a misunderstanding. If we add dilute caustic soda to a silver nitrate solution, we get silver oxide and not silver hydroxide. On the other hand, silver oxide and water are used by the organic chemists as equivalent to silver hydroxide. Either it occurs in solution or a solution of silver oxide has the properties of silver hydroxide, which comes to about the same thing. If we add dilute caustic soda to a copper sulphate solution, we get the bluish precipitate which is commonly called cupric hydroxide. If we spent our lives always in hot water, we should not know this substance because addition of caustic soda to a hot copper sulphate solution precipitates the black oxide. If we boil wool with a solution of a copper salt, the fiber turns green. According to Knecht, Rawson and Loewenthal[1] it is conclusively shown that a hydrate is not formed "in mordanting wool with copper salts. The fiber assumes a green color, but copper hydrate when boiled is at once dehydrated and transformed into black copper oxide. If copper hydrate had been formed, the fiber would be black, whereas it is green, and remains so even after prolonged boiling."

This is a fatal illustration. It is true that cupric hydroxide does usually turn black when boiled with water; but Tommasi[2] has shown that this is not the case when one adds a little manganous sulphate to the solution. Under these conditions the solution can be boiled for a long time without causing the appearance of black copper oxide. This is a very

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[1] "A Manual of Dyeing," second edition, **1**, 59 (1910).

[2] Bull. Soc. chim. Paris, [2] **37**, 197 (1882); Comptes rendus, **99**, 37 (1884).

interesting experiment. In some way the manganese salt increases the stability of the cupric hydroxide so that it does not blacken at 100°. If a manganese salt can do this, there is no reason why the wool fiber should not do the same, as apparently it does. There is no apparent reason why we should treat cupric hydroxide in one way and silk dyed with magenta in another way. I therefore conclude that silk stabilizes the color base of fuchsine, that wool stabilizes copper hydroxide, and that a manganous salt also stabilizes cupric hydroxide. In the paper of Finch[1] we have another type of stabilization. An instable cupric oxide jelly becomes stable in presence of a limited amount of sulphate. The experiments of Bunce and Finch[2] show that a certain concentration of acetate is necessary in order to stabilize a chromic oxide jelly. Because a substance is soluble in water does not mean that that substance will dissolve readily when adsorbed by charcoal. Because a color base is instable in solution does not mean that it is instable when adsorbed by silk.

The point has been made that alcohol will remove all the color from silk that has been dyed in an ammoniacal fuchsine solution more readily than from silk that has been dyed in an acetate solution.[3] Assuming this statement to be true, it should be noted that it is not necessary to assume that silk always takes up the free color base alone, because it does so under certain circumstances. We have already seen that more dye is taken up in presence of a readily adsorbed anion or that a given amount of dye is held more firmly in presence of a readily adsorbed anion. It seems to me therefore not impossible that one may get a more permanent dyeing with rosaniline acetate, for instance, than with the free base. One ought to have more definite experiments on this point before coming to a final conclusion.

Another point on which experiments are needed is as to

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[1] Jour. Phys. Chem., 18, 26 (1914).

[2] Ibid., 17, 769 (1913).

[3] Schwalbe: Ahrensche Sammlung chemisch-tehnischer Vorträge, 12, 120 (1907).

beneficial effect of magnesium sulphate when dyeing with crystal violet.[1] "It has long been remarked that woolen goods dyed with aniline colors, and treated with Epsom salts, will stand the action of soap and soda, and the dressing process generally, better than when not so treated or than when treated with any other substance. Dr. Reimann advises the use of Epsom salts in yarns to be dyed violet. By the action of the soda, the magnesium salt is decomposed, with separation of insoluble magnesium compounds, which exert no action upon the coloring matter; any alteration in the color by the alkali is thus prevented."

Professor W. J. Hale of the University of Michigan called my attention to a paper on the constitution of aniline black by Green and Wolff[2] in which these authors say: "It is interesting to note that whereas emeraldine, nigraniline, and aniline black are all, when produced in substance, easily soluble in 80 percent acetic acid, they cannot be extracted from the fiber by this solvent, but remain completely undissolved. That this must be attributed to some state of combination existing between the fiber and the dyestuff is proved by the fact that after removal from the fiber they are all obtained in a soluble condition. The removal is effected by dissolving the cotton in cold concentrated, sulphuric acid and pouring into water. The emeraldine or aniline black is obtained as a voluminous precipitate, which is filtered off, thoroughly washed, and basified by boiling with ammonia. The products thus obtained give the same reactions as the compounds prepared in substance." Green and Wolff attribute the insolubility to a reaction between the cotton and the dye; but it is evident that this is analogous to the case of crystal violet and charcoal. There has been no change in the aniline black and as soon as the cotton is removed, the normal properties of aniline black are recovered.

In the discussion of basic dyes and in the preceding paper

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[1] Jour. Chem. Soc., **27**, 500 (1874).

[2] Jour. Soc. Dyers, **19**, April (1913).

on acid dyes, I have ignored completely the question whether the dyes formed true solutions or not. Teague and Buxton[1] found that methylene blue, chrysoidine, safranine, eosine, Bismarck brown, and alizarine red dialyzed readily through parchment at ordinary temperatures and were only slightly colloidal if at all. Nile blue, aniline blue, and alkali blue did not dialyze at ordinary temperatures but did somewhat at 37°. They are classed as highly colloidal. Congo red, azo blue, and night blue did not dialyze even at the boiling point and are considered as completely colloidal. Others[2] class methylene blue, picric acid, malachite green, eosine, fluoresceine, auramine, and alizarine red as true solutions; methyl violet, crystal violet, Capri blue, Nile blue, neutral red, Helvetia blue, and rhodamine 6 G as partly colloidal; fuchsine, night blue, roccelline, and the direct cotton colors as completely colloidal.

The theory outlined in these papers is not concerned with the question whether the dyes form true solutions or colloidal ones. As far as the qualitative side is concerned, and that is the important thing at present, the general relations all hold whether the dye forms a true solution or not. It seems to me quite probable that the quantitative change in adsorption with varying acidity or alkalinity can only be answered after we decide whether a given dye does or does not form a true solution. For the moment, however, all that interests me is the outlining of a working theory of dyeing. The quantitative details can be filled in at any time.

The general results of this paper are:

1. A basic dye is taken up most readily in an alkaline solution but may be taken up in a neutral or acid solution.

2. A readily adsorbed anion increases the amount of a basic dye taken up.

3. A readily adsorbed cation decreases the amount of a basic dye taken up.

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[1] Zeit. phys. Chem., 60, 479 (1907).

[2] Cf. Pelet-Jolivet: "Die Theorie des Färbeprozesses," 33 (1910).

4. Since the sulphuric acid radical is adsorbed readily by wool, addition of sulphuric acid will cause more of a basic dye to be taken up by wool than addition of an equivalent quantity of hydrochloric acid or than addition of isohydric hydrochloric acid.

5. Addition of sodium sulphate to a dye-bath will cause more of a basic dye to be taken up by wool.

6. The theories in regard to the color bases of fuchsine and crystal violet have been discussed at length.

7. Freundlich's assumption of a condensation product of an imine base is unnecessary and undesirable.

8. When silk is dyed red from a colorless, ammoniacal solution of magenta, the only argument against the color being due to the free color base is the instability of this latter in solutions.

9. Manganous sulphate stabilizes cupric hydroxide so that it does not blacken when boiled with water.

10. Wool stabilizes cupric hydroxide so that the fiber remains green even after the prolonged boiling.

11. Silk stabilizes the color base of magenta. Because this base is instable in solution is no reason why it should be when adsorbed by silk.

12. There is nothing in the theory as outlined to prevent the color being faster when silk is dyed with a fuchsine salt than when dyed with the free color base. The evidence is not conclusive as to the existence of such a difference.

13. It is possible, though not proved, that magnesia stabilizes the color base of methyl violet.

14. Cotton causes adsorbed aniline black to become insoluble in 80 percent acetic acid. If the cotton is removed, the aniline black recovers its so-called normal properties.

15. So far as the qualitative side of the present theory of dyeing is concerned, it makes no difference whether a given basic or acid dye forms a true solution or a colloidal one.

The third paper of the series will deal with mordants. Owing to press of other work, the appearance of the next article is likely to be somewhat delayed.

Cornell University

THE DETERMINATION OF THE VELOCITY OF REACTIONS IN SOLUTION FROM THE CHANGE IN DENSITY[1]

BY ERNEST ANDERSON AND J. L. HOLDEN

Many reactions in solution take place with considerable change in density. It should be possible to determine the velocity of such reactions from a study of the density. There are probably three reasons why this density method for determining the velocity of reactions in solution has not been used to any extent. First, the change in density, in many such reactions, is comparatively slight. Second, while it is possible to determine the density of solutions to a high degree of accuracy, the process is slow. Third, other very accurate physical and chemical methods have been developed for this purpose. As soon as a direct method is perfected for obtaining the density of solutions very rapidly to the seventh decimal place, undoubtedly the density method will be used for determining the velocity of some reactions.[2]

As an illustration of the density method for determining reaction velocities the authors have used the inversion of cane sugar. It is well known that a solution of cane sugar increases in density as it inverts. A number of chemists have studied this change in density, and the data on it are numerous. However, no one seems to have determined accurately the velocity of this change in density.

In the investigation three acids, oxalic, sulphuric, and

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[1] Contribution from the Massachusetts Agricultural College.

[2] K. Koelichen: Zeit. phys. Chem., 33, 154 (1900), has used the dilatometric method in measuring the velocity of splitting of diacetone alcohol into two molecules of acetone by bases and salts. G. Galeotti: Zeit. phys. Chem., 76, 105 (1911); 80, 241 (1912) has used the dilatometric method for determining the velocity of inversion of cane sugar and of other reactions.

A. Benrath (Zeit. phys. Chem., 67, 501 (1909)) has made an accurate study of the density changes in the following reactions: Inversion of cane sugar, catalysis of certain esters by acids; esterification of certain acids and saponification of some esters.

hydrochloric, were used, all in normal solution. The following table gives in column (I) the constants found by the density method, and in column (II) the constants found by the optical method.

Oxalic acid		Sulphuric acid		Hydrochloric acid	
I	II	I	II	I	II
0.0007403	0.0008525	0.002270	0.002435	0.005106	0.004944
0.0008370	0.0009356	0.002485	0.002529	0.004992	0.005059
0.0007668	0.0009061	0.002467	0.002759	0.005153	0.005176
0.0007905	0.0008894	0.002599	0.002104	0.005338	0.005183
0.0008183	0.0008908	0.002387	0.002638	0.005087	0.005086
—	0.0009012	0.002411	0.002452	0.005118	0.005126
—	0.0008923	0.002362	0.002588	—	0.005159

Experimental Part

In each determination a 1000 cc flask containing 500 cc of a 20 percent cane sugar solution, *i. e.*, 20 grams of sugar made up to 100 cc with water, is placed in the thermostat at 25° C. At the same time 500 cc of a normal acid and a dry, accurate, 50 cc specific gravity bottle[1] are placed in the thermostat. When the solutions have reached the temperature of the thermostat the acid is poured rapidly in to the sugar, the whole shaken well, returned to the thermostat and the specific gravity bottle filled by means of a pipette. The thermometer, which serves as a stopper, is then inserted, and the drop on top of the side neck is removed with a towel, the time being recorded as the drop is removed. The specific gravity bottle is then taken out of the thermostat, allowed to stand a short time until the solution has contracted down the narrow neck and the whole weighed.

After weighing the specific gravity bottle and solution, the solution is thrown out, the bottle washed, dried with alcohol and ether and an air stream, and returned to the

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[1] The specific gravity bottle used had a thermometer for stopper and a narrow side neck fitted with a cap. The bottle used with hydrochloric acid had a volume of 50.0507 cc at 25° C while the bottle used with oxalic and sulphuric acids had a volume of 50.6989 cc.

thermostat. In the course of about 90 minutes the bottle is again filled and weighed as above described. This is repeated at intervals of 30 to 60 minutes until 8 or 10 readings have been made. The solution is then allowed to stand until there is no further change in the weight of the bottle full of solution. If the second reading is made in less than 90 minutes after the first reading the constant does not agree well with the other constants. This point was not investigated closely.

In order to study the change in density at different rates three acids were used, oxalic, sulphuric and hydrochloric, all in normal solution. At the same time, for the sake of comparison, the speed of inversion of the same sugar solution was determined by the polariscope.

In calculating the constant it is necessary to know only the change in weight of the bottle full of solution and the constants given above are calculated in that way. The same constants are obtained if the density is calculated from the weights and the constant then calculated from the density.

Data

In the following tables, W in each case is the weight of the bottle full of solution, or the reading of the polarimeter; T is the corresponding time; t is the time in minutes from the first reading; $A - X$ is the end reading minus the reading at time t; A is the end reading minus the first reading; K is the constant given by the monomolecular reaction formula

$$K = \frac{2.3025}{t} \log \frac{A}{A - X}.$$

CONSTANTS BY THE DENSITY METHOD

(*a*) For oxalic acid

W	T	t	A — X	K
83.6915	8.26	0	960	—
83.7012	10.50	144	863	0.0007403
83.7083	12.16	230	792	0.0008370
83.7157	2.45	379	718	0.0007668
83.7196	3.44	438	679	0.0007905
83.7242	4.55	509	633	0.0008183
83.7875	End	—	—	—

(*b*) For sulphuric acid

83.9420	8.59	0	973	—
83.9576	10.16	77	817	0.002270
83.9706	11.19	140	687	0.002485
83.9758	11.52	173	635	0.002467
83.9965	2.15	316	428	0.002599
84.0003	3.21	382	390	0.002387
84.0065	4.30	451	328	0.002411
84.0100	5.27	508	293	0.002362
84.0393	End	—	—	—

(*c*) For hydrochloric acid

87.6774	10.27	0	826	—
87.7127	12.16	109	473	0.005106
87.7285	1.40	193	315	0.004992
87.7345	2.15	228	255	0.005153
87.7418	3.12	285	182	0.005338
87.7465	4.23	356	135	0.005087
87.7510	5.40	433	90	0.005118
87.7600	End	—	—	—

CONSTANTS BY THE OPTICAL METHOD[1]

(*a*) For oxalic acid

W	T	*t*	A — X	K
+39.00	7.28	0	50.7	—
+35.50	8.52	84	47.2	0.0008525
+34.00	9.19	111	45.7	0.0009356
+33.00	9.47	139	44.7	0.0009061
+32.00	10.15	167	43.7	0.0008894
+30.50	10.54	206	42.2	0.0008908
+29.40	11.21	233	41.1	0.0009012
+28.50	11.48	260	40.2	0.0008923
+24.00	2.01	393	35.7	0.0008921
+22.60	2.59	451	34.3	0.0008664
+20.0	4.05	517	31.7	0.0009080
—11.7	End	—	—	—

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[1] A saccharimeter, reading in percent, was used. For oxalic and hydrochloric a 2 dm tube was used while for sulphuric a 1 dm tube was used.

(*b*) For sulphuric acid

+18.50	8.49	0	24.5	—
+17.00	9.15	26	23.0	0.002435
+15.00	9.50	61	21.0	0.002529
+11.50	10.51	122	17.5	0.002759
+10.50	11.16	147	16.6	0.002104
+ 9.40	11.45	176	15.4	0.002638
+ 8.20	12.32	223	14.2	0.002452
+ 6.50	1.09	260	12.5	0.002588
+ 5.80	1.44	295	11.8	0.002477
+ 5.00	2.16	326	11.0	0.002457
+ 3.40	2.56	367	9.4	0.002610
+ 2.00	4.03	434	8.0	0.002578
— 6.00	End	—	—	—

(*c*) For hydrochloric acid

+36.40	10.46	0	48.4	—
+28.50	11.22	36	40.5	0.004944
+19.80	12.09	83	31.8	0.005059
+12.80	12.53	129	24.8	0.005176
+ 5.70	2.00	194	17.7	0.005183
+ 2.50	2.43	237	14.5	0.005086
+ 0.00	3.20	272	12.0	0.005126
— 3.50	4.25	337	8.5	0.005159
—12.00	End	—	—	—

THE VISCOSITY OF BINARY MIXTURES

BY EUGENE C. BINGHAM

In 1905 Jones and Bingham[1] advanced the hypothesis that in binary mixtures fluidities are normally additive. The prevailing assumption had been that viscosities are additive, but it was seen that if fluidities are additive viscosities cannot be. There was theoretical justification[2] for the newer hypothesis and the existing experimental data were in its favor,[3] for whereas it had been repeatedly noted that "the viscosity of a mixture of miscible and chemically indifferent liquids is rarely, if ever, under all conditions, a linear function of the composition"[4] it was found that the *fluidity* of such a mixture is much more nearly a linear function of the composition.

Binary mixtures do not afford the best opportunities for testing the validity of the above hypothesis, since so many liquids are associated and do not fulfil the requirement of being "chemically indifferent" to each other; so that, on mixing, either the association may break down causing a rise in the fluidity or a more or less feeble chemical combination may take place causing a drop in the fluidity. During the past nine years the author and his co-workers[5] have been engaged in accumulating other lines of evidence and in working out some of the consequences of the hypothesis so long as the truth of the fundamental hypothesis should remain unquestioned. Recently, however, James Kendall[6] working in the Nobel Institute of Physical Chemistry under the direction

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[1] Am. Chem. Jour., 34, 481 (1905). Lees [Phil. Mag., [6] 1, 128 (1901)] considered the fluidity formula for mixtures but discarded it because he found an empirical formula which better accorded with his data.

[2] Jour. Am. Chem. Soc., 33, 1257 (1911).

[3] Am. Chem. Jour., 35, 195 (1906).

[4] Thorpe and Rodger: Jour. Chem. Soc., 71, 374 (1897).

[5] Bibliography and summary of results, Phys. Rev., 35, 407 (1912).

[6] Meddelanden K. Vetenskapsakademien Nobelinstitut, 2, No. 25 (1913).

of Arrhenius has reached the conclusion that "the logarithmic viscosity (or fluidity) of a solution is the characteristic additive property, and not these quantities themselves."

Kendall reached this conclusion by obtaining the viscosity data for as many "normal" mixtures as possible and then comparing the observed values with those calculated on the various hypotheses that (1) viscosities are additive when volume concentrations are employed, (2) logarithmic viscosities are additive when volume concentrations are employed, (3) fluidities are additive when volume concentrations are employed, (4) fluidities are additive when weight concentrations are employed, and (5) logarithmic viscosities (or fluidities) are additive when molecular concentrations are employed. He finds that the last gives better agreement and on this fact he bases the conclusion that the logarithmic viscosity (or fluidity) of a solution is the characteristic additive property.

It is highly important that it be soon decided once for all whether viscosity, fluidity, or the logarithm of the fluidity (or viscosity) is to be regarded as the characteristic additive property in a given case. Viscosity, as a property of matter, is of fundamental importance in many lines of investigation. It is absolutely necessary that we have a clear understanding of the nature of viscosity before we can hope to obtain a satisfactory understanding of conductivity, migrations of ions, rate of diffusion, rate of crystallization, and of the nature of colloidal solutions; and we may reasonably expect to find viscosity related in an important manner to volume, vapor-pressure, association, hydration, and other properties. Discussion of this subject therefore seems desirable.

Admitting a slight numerical superiority for the empirical logarithmic formula, is one justified in making an inference on account of it in regard to a fundamental physical relationship? As in the expansion of gases, may it not be that the ideal case is never realized and that, moreover, the exceptions are for the most part in *one* direction? Whatever the answer, the importance of the law which applies strictly to the ideal case only, like Boyle's law, is not lessened thereby.

There is a further objection to Kendall's conclusion, which is more serious. He has applied his test to so-called "normal" curves only, and following Dunstan's[1] classification, Kendall regards all viscosity curves as normal which do not have a maximum or minimum. This classification places all mixtures in three categories which are quite sharp but also quite arbitrary, since, as has already been pointed out,[2] the occurrence of a maximum or minimum is an accidental circumstance, depending very largely on the nearness to equality in the viscosities of the components of the mixtures. If the viscosities of the components are exactly equal, the feeblest sort of chemical combination will be sufficient to produce a maximum; and on the other hand, a large amount of chemical combination may be insufficient to produce a maximum if the viscosities of the components are very unequal.[3]

We shall now attempt to prove that the method of selecting the data used in the comparison described above would have tended to produce the result noted by Kendall even if fluidities are normally additive. In Fig. 1 *AFB* is drawn to represent a linear fluidity curve, abscissas representing concentrations and ordinates fluidities. If this were the normal fluidity curve, supposed to be given by unassociated and chemically indifferent liquids, the normal viscosity curve obtained by plotting the reciprocals of the fluidities would be *afb*, which is part of an equilateral hyperbola whose asymptotes are *CD* and *CE*, the point *C* being the point where the fluidity curve cuts the X-axis. On the other hand, if the viscosities are additive, the normal viscosity curve is of the form *aVb*, so it is seen that the viscosity of any mixture is smaller, if the fluidities are additive, than would be expected,

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[1] Jour. Chem. Soc., 91, 83 (1907).

[2] Phys. Rev., [2] 1, 108 (1913).

[3] Kendall himself notes that Dunstan's classification is not altogether satisfactory, for "even where the curve of the viscosity appears to be of the normal type, changes of state may have occurred in the mixture which are not sufficient to bring about a maximum or a minimum point." For an attempt to obtain a more natural classification see Zeit. phys. Chem., 83, 660 (1913).

if viscosities were additive. It can be proved[1] mathematically that this must invariably be the case except when the fluidities of the components are identical, in which case the difference becomes zero. Now if logarithmic viscosities (or fluidities) are additive, the normal viscosity curve will be *alb*, which is intermediate between the other two curves; and it can be shown that if logarithmic fluidities are additive, the viscosity of a mixture must always be greater than would be expected on the hypothesis that fluidities are additive and less than would be expected on the hypothesis that viscosities are additive.

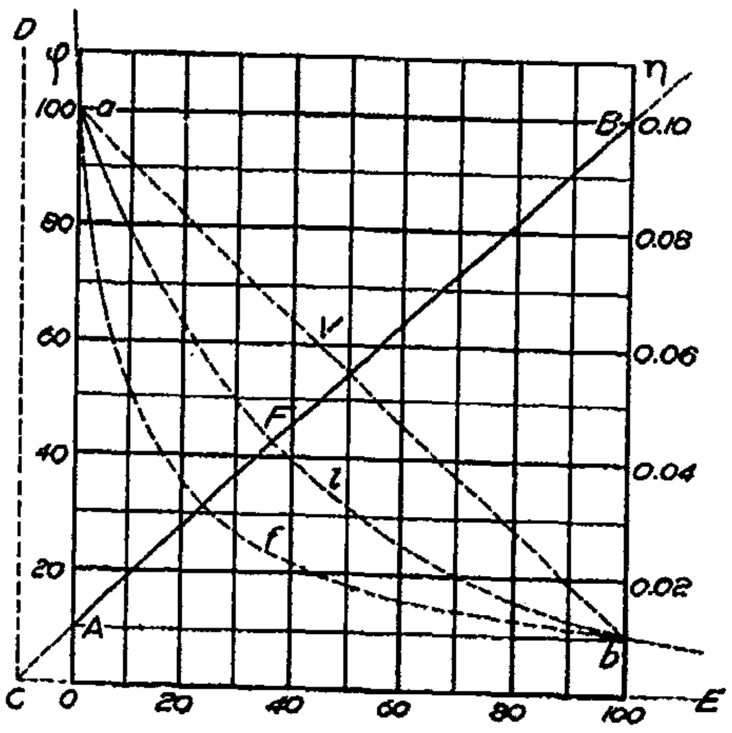

Fig. 1

Were liquids usually chemically indifferent and unassociated, there would be no difficulty in deciding which one of these hypotheses is correct. Unfortunately for our purpose, in the greater number of mixtures there is a change of temperature and volume on mixing and the cause of these changes also affects the viscosity and other properties. When there is a considerable contraction and heat evolution on mixing, there seems to be an invariable increase in the viscosity, and on the other hand, when there is expansion and heat absorption on mixing there is a lowering of the viscosity. In

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[1] Jour. Am. Chem. Soc., 33, 1261 (1911); cf. Phys. Rev., 35, 411 (1912).

taking the viscosity curves which show neither maximum nor minimum as his material for comparison, Kendall practically took the curve *aVb* as his normal curve, since it lies half way between the two extremes, where a maximum or minimum occurs and yet the object of the investigation was to *discover* which curve should be considered normal. Having taken as normal those curves which approximate to *aVb* instead of to *afb* or *alb*, the hypothesis that logarithmic fluidities are additive is placed at a disadvantage and the hypothesis that fluidities are additive is placed at a still greater disadvantage. It would have been at least as logical to have taken as normal those *fluidity* curves which do not give a maximum or minimum and the result would certainly have been different, although of no value, because the case would have been prejudged in the choice of the data. The proper definition of a *normal curve*, to be as free as possible from objection, is *the curve given by substances which mix without volume or heat change.* This definition does not prescribe whether viscosities, fluidities, or other functions of the viscosity are to be compared and the question whether weight, volume, or molecular concentrations are to be used is likewise left open.

If fluidities are really additive, Kendall's choice of data gave preference to mixtures in which there is heat evolution and contraction since the corresponding increase in viscosity would correct the sagging of the curve *afb*. Thus while this method of choosing the data established a prejudice in favor of the hypothesis that viscosities are additive, yet the data are against that hypothesis, and the utmost that was accomplished was the shifting of the average curve, so that it lies between those expected on the two extreme hypotheses and somewhere near the intermediate curve given by the hypothesis that logarithmic viscosities are additive.

From what has been said it seems probable that Kendall has considered a greater number of mixtures where contraction and heat evolution take place than of the opposite kind; certainly examples of this kind are more common in the literature. Contraction and heat evolution seem to be quite common in water mixtures, for example, and it is quite possible that these effects are due to a feeble chemical combination which is more pronounced and common than the opposite effect of dissociation. I have elsewhere[1] attempted to show that the conditions in ordinary mixtures are quite analogous to those in electrical conduction when the resistances are in parallel, *i. e.*, the fluidities, like the conductivities, are additive or $\varphi = m_1\varphi_1 + m_2\varphi_2$ where m_1 and m_2 represent the fractions of the total *volume* occupied by each of the components, having fluidities of φ_1 and φ_2, respectively. When under certain conditions the mixture is not homogeneous as in certain emulsions, the conditions are analogous to those in electrical conduction when the resistances are in series, *i. e.*, the viscosities are additive or $\eta = m_1\eta_1 + m_2\eta_2$. Thus the fact is accounted for[2] that when a homogeneous mixture is cooled below its critical solution temperature, the fluidity decreases quite unexpectedly. It is not apparent that so simple an explanation could be obtained if logarithmic fluidities are the characteristic additive property.

When conductors are arranged so as to be in parallel and in series simultaneously, a checkerboard arrangement results. Lees[3] has shown that for such an arrangement of viscous substances the logarithm of the resulting fluidity is equal to the logarithms of the components multiplied by their respective fractions of the total *volume*, or

$$\log \varphi = m_1 \log \varphi_1 + m_2 \log \varphi_2.$$

The author believes[4] that ordinarily this condition is a fleeting one and that after a time a homogeneous mixture results in which the fluidities are strictly additive. But in any case, as Lees has clearly pointed out, volume percentages must be employed and not molecular percentages

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[1] Phys. Rev., 35, 407 (1912).
[2] Jour. Am. Chem. Soc., 33, 1257 (1911).
[3] Phil. Mag., [6] 1, 128 (1901).
[4] Phys. Rev., 35, 409 (1912).

as Kendall has proposed. Kendall states[1] "A molecular formula has not been proposed. This is certainly strange, since from first principles the viscosity is a function of the molecular concentration, 'viscosity being essentially the frictional resistance encountered by the molecules of the solution in moving over one another.'" It is undoubtedly true that the size of the molecules determines the fluidity of each component, but it is difficult to see how the size of the molecules enters a second time into the calculation when two or more components are combined in a mixture.

Finally there are various other lines of evidence in favor of the hypothesis that fluidities are additive, which at least have not yet been shown to be *equally in favor* of the hypothesis that logarithmic fluidities are additive. For example, suspensions of finely divided solids in liquids in which they are insoluble give fluidities[2] which are a *linear* function of the volume concentration. Moreover these curves converge toward a definite zero of fluidity. The viscosity and the logarithmic fluidity curves are not linear and they do not meet except at infinity.

A. Batschinski[3] has very recently discovered that the volume of a liquid is a linear function of its fluidity $v = a + b\varphi$ where a and b are constants characteristic of the given liquid. This would be a very surprising relation, if fluidities were not additive.

Making use of the hypothesis that fluidities are additive it has been found[4] possible to calculate the association of associated substances and to obtain values which are in excellent agreement with values calculated by other methods.

It is probable that dissociation and combination play an unexpectedly common and important rôle in mixtures and solutions. It has been repeatedly pointed out that there is almost always some heat and volume change when liquids

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[1] Page 3.

[2] Am. Chem. Jour., 46, 278 (1911); cf. Phys. Rev., 35, 419 (1912).

[3] Ann. Soc. d'encour. sc. exper. et de leurs applic. Suppl., 3, 1913.

[4] Zeit. phys. Chem., 66, 28 (1909); cf. Phys. Rev., [2] 1, 106 (1913).

are mixed, which has been taken as an evidence of chemical action. Under these circumstances, it is well-nigh useless to attempt to find an empirical formula to fit all cases. It seems more logical to first discover what is the characteristic additive property. All cases which then do not fit the accepted formula—perhaps very few will fit it—will be explained on the basis of dissociation or combination or both. If these chemical changes are subject to the familiar chemical laws of Definite and Multiple Proportions and Mass Action, then it may prove a comparatively simple matter from the fundamental fluidity (or other) formula and the affinity constants to calculate the fluidity of any mixture at any temperature, knowing the fluidities of the components. Work by the author and his co-workers along this line has already yielded some very promising results.[1] The formation of a so-called "hydrate" or other feeble combination is not to be lightly assumed as a pure matter of convenience. The trouble in the past has been not in a lack of evidence but that the evidence has been confusing. When two liquids were mixed, the contraction in volume and heat evolution were taken as evidences of chemical combination, and the composition of the hydrate was taken to be that of the mixture in which the contraction and heat evolution were a maximum. The maximum in the viscosity curve was likewise taken to indicate the composition of a hydrate, but this hydrate was different and moreover its composition seemed to vary with the temperature. Naturally when the testimony of the different properties upon this important question was so greatly at variance, chemists were forced to regard the whole question as open. It is a satisfaction therefore to be able to state that in the cases which have been carefully investigated, the maximum deviation from the linear fluidity-volume concentration curve is found in the same mixture which shows the greatest heat and volume changes on mixing. In the case of

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[1] Zeit. phys. Chem., 83, 662 (1913).

ether and chloroform,[1] for example, this mixture also corresponds exactly to the formula $C_4H_{10}O.CHCl_3$, and furthermore the vapor-pressure curves of these mixtures give evidence of the formation of the same complex. Thus the way seems open for a considerable extension of our conceptions in regard to chemical combination and the difficult problem of hydration in solution.

Richmond College
Richmond, Va.
June 30, 1913

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[1] Loc. cit.

THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN PEROXIDE

FIRST PAPER

BY J. HOWARD MATHEWS AND HARRY A. CURTIS

Introductory

It has been known for a long time that light is a factor in the ordinary slow decomposition of hydrogen peroxide. In 1879, Downes and Blunt[1] found that an 8 percent solution of hydrogen peroxide was entirely decomposed after a ten months' exposure to sunlight, while a similar solution, kept in the dark, was much more stable. This accelerating influence of light was also noted by D'Arcy[2] in his investigation of the electrical phenomena accompanying the decomposition of hydrogen peroxide. The decomposition of hydrogen peroxide in the presence of blood serum salts was investigated by Kistiakowsky,[3] who came to the conclusion that the light, in this case, acts as an indirect catalyst through the formation of a "photo-colloid" from the blood serum salts, which then decomposes the peroxide. Supporting this view is the fact that the reaction continues at the same rate in the dark after the solution has been once illuminated. In 1907, Thiele[4] reported the decomposition of hydrogen peroxide by the light from a mercury arc, and three years later Tian[5] measured the rate of this reaction in ultraviolet light, finding it to be a reaction of the first order. During the summer of 1913, while the experiments which we describe below were in progress, two papers by Henri and Wurmser[6] on the photolysis of hydrogen peroxide appeared. The first of these deals with the decomposition in monochromatic light of various wave lengths,

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[1] Nature, **20**, 521 (1879).

[2] Phil. Mag., [6] 3, 42 (1902).

[3] Zeit. phys. Chem., **35**, 431 (1900).

[4] Zeit. angew. Chem., **22**, 2472; Ber. chem. Ges. Berlin, **40**, 4914 (1907).

[5] Comptes rendus, **151**, 1040 (1910).

[6] Ibid., **157**, 126, 284 (1913).

the energy absorbed at each wave length being measured by a thermopile and galvanometer. The second paper concerns the negative catalysis of the photochemical reaction by various substances.

Source of Light

As a source of light we have employed a "uviol lamp" (mercury arc in Schott & Gen. "Uviol B" glass) running on a 110 volt circuit. In series with the lamp were placed a rough rheostat, a small sliding-contact resistance coil, the usual inductance spool to compensate for small variations of current, and an ammeter. A volt-meter was connected across the terminals of the lamp. Since there is a considerable "kick" from the inductance spool when the lamp goes out, and this sooner or later burns out the volt-meter, it was found best to include a key in the volt-meter circuit, making contact only for the instant required to read the instrument.

In order to get constant illumination it is necessary to keep the potential drop across the lamp constant, and this is not easy to do if the lamp is exposed to the air. We found it much better to jacket the lamp in a uviol-glass tube and then keep the temperature constant by drawing air through the jacket. With this arrangement the resistance of the lamp becomes constant a few minutes after lighting it, and the regulating is very easy. The temperature inside the jacket may be kept considerably above room temperature—we use 80–90°—and the tendency for mercury globules to fog the sides of the lamp thereby is much lessened.

Reaction Chamber

A tube of quartz, closed at one end with paraffin, served as the reaction chamber. This tube was jacketed in a uviol-glass tube and kept at constant temperature by pumping water from a thermostat through the jacket. The quartz tube carried a wooden pulley at its upper end, and was rotated on its axis at constant speed by a small electric motor and pulley system. This rotation secures uniform illumination of all sides of the reaction tube, and, together with the mixing of the solution caused by the bubbles of oxygen rising from the decomposing peroxide, accomplished a very fair stirring. The reaction tube was placed at a distance of 5 cm (nearest sides) from the lamp, and parallel to it. The arrangement of the apparatus is shown diagrammatically in Fig. 1.

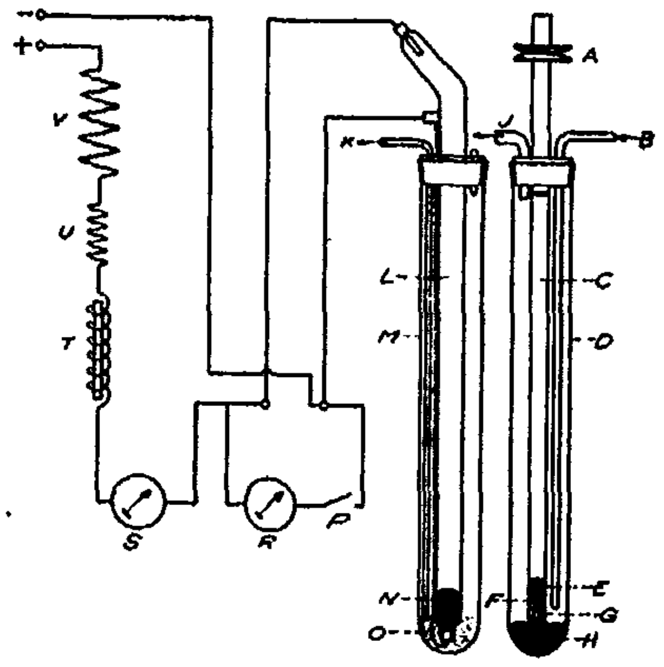

Fig. 1

A—Pulley for rotating quartz tube.
B—Entrance for water from thermostat.
C—Quartz reaction tube.
D—Uviol-glass jacket.
E—Paraffin.
F—Cork.
G—Brass spindle.
H—Cork.
J—Exit for water returning to thermostat.
K—Tube drawing air through lamp jacket.
L—Uviol lamp.
M—Uviol-glass jacket.
N—Mercury in lamp.
O—Glass wool.
P—Key in the volt-meter circuit.
R—Volt-meter.
S—Ammeter.
T—Inductance spool.
U—Small sliding contact resistance.
V—Rough rheostat.

Thermometers in both jackets, thermostat, and pulley system for rotating reaction tube not shown in diagram.

The Hydrogen Peroxide Solution

Distilled water of conductivity approximately 1.5 × 10^{-6} mhos was prepared and stored in a quartz flask. Merck's 30 percent "perhydrol, absolut säurefrei, chemisch rein" was then poured directly from its paraffin container into the water to give the strength of solution desired. Fifty-five cc of this solution were poured into the reaction chamber, this amount giving a column 60 cm high in the tube.

It is well known that the alkalies from glass affect the rate of decomposition of hydrogen peroxide.[1] By using only quartz as a container for the peroxide, we have avoided the possible catalytic effect from this source.

The peroxide content of the solution was determined by titrating with potassium permanganate solution in the presence of sulphuric acid. In the first experiments, the sampling was done with a capillary pipette, but later this was discarded and the sample withdrawn for titration was transferred to a weighing bottle containing dilute sulphuric acid and accurately weighed. By using about a half-gram sample, and a permanganate solution *N*/20, the error of analysis was less than 0.01 percent on a 3 percent peroxide solution.

Rate of Decomposition

Without illumination, the rate of decomposition was very slow at temperatures below 50°. The reaction begins immediately upon illumination and proceeds smoothly. Upon extinguishing the lamp, the rate of decomposition again becomes very slow. Fig. 2 shows graphically the effect of

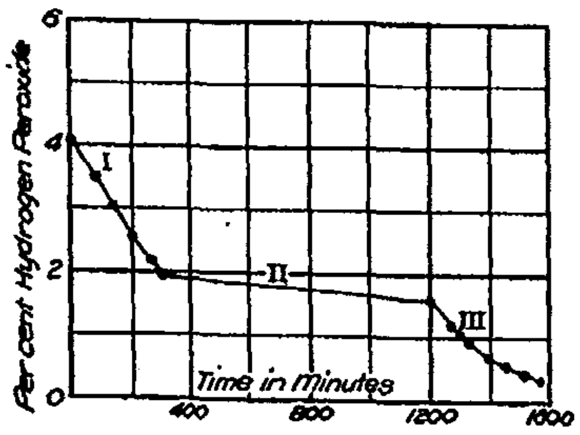

Fig. 2

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[1] See, for example, Walton and Judd: Zeit. phys. Chem., 83, 315 (1913).

illumination. Curve I represents the rate of decomposition with illumination, Curve II shows the rate when the lamp is extinguished, and Curve III the rate upon again illuminating.

We find no evidence of an inductance effect, either at the beginning or at the end of the illumination; an inductance period of less than two minutes would, however, escape our notice under the experimental conditions established.

Order of the Reaction

In agreement with the results of Tian and of Henri and Wurmser, we find that the photolysis of hydrogen peroxide is a reaction of the first order, as the following data, represented by Fig. 3, show:

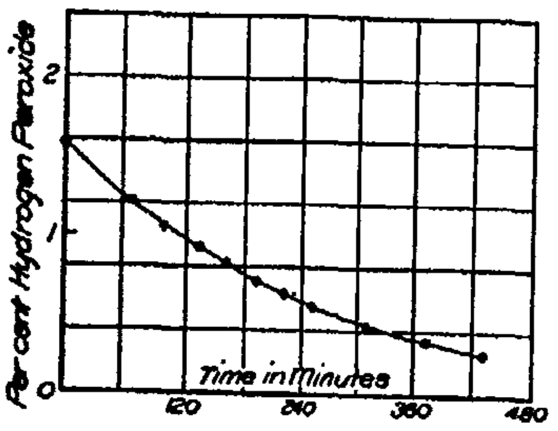

Fig. 3

Table I

Time (Min.)	Per cent H_2O_2	K (for first order)
0	1.58	—
70	1.21	0.0038
100	1.06	0.0040
132	0.93	0.0041
160	0.83	0.0041
191	0.71	0.0042
220	0.63	0.0042
252	0.55	0.0042
310	0.44	0.0041
373	0.34	0.0042
432	0.26	0.0042

Temperature Coefficient of the Reaction

We find the temperature coefficient of the reaction to be about 1.5, as the following data show:

TABLE II

Temperature 35°

Time (Min.)	cc $KMnO_4$	K′ (for first order)
0	74.26	—
30	71.10	0.0015—
60	68.9	0.0011—
90	66.3	0.0013—
120	63.7	0.0013+
150	60.9	0.0015
182	58.3	0.0014—
214	55.7	0.0014+
		Average value K′ = 0.00136

TABLE III

Temperature 45°

Time (Min.)	cc $KMnO_4$	K″ (for first order)
0	51.2	—
20	49.2	0.0020
40	47.2	0.0021—
58	45.4	0.0021+
137	38.0	0.0022+
158	36.4	0.0020+
		Average value K″ = 0.0021—

For the 10° interval:

$$\frac{K''}{K'} = 1.54$$

This ratio was checked by the following duplicate experiment:

TABLE IV

Temperature 21°

Time (Min.)	cc $KMnO_4$	K′ (for first order)
0	41.4	—
42	40.3	0.0006
76	39.2	0.0008
116	38.1	0.0007
157	37.0	0.0007
		Average value K′ = 0.0007

TABLE V

Temperature 35.5°

Time (Min.)	cc $KMnO_4$	K″ (for first order)
0	35.9	—
34	34.5	0.0012
70	33.2	0.0011
130	30.7	0.0013
166	29.5	0.0011
		Average value K″ = 0.0012

For 10° interval:

$$\frac{K_{t+10^\circ}}{K_t} = 10^{\log\left(\frac{0.0012}{0.0007}\right)^{\frac{10}{14.5}}} = 1.45.$$

It is probable that these ratios are a trifle high due to the slight increase in the natural rate of decomposition (*i. e.*, without illumination) at the high temperature. This effect is, however, small compared with the photochemical decomposition.

Negative Catalysis of the Light Reaction

It is an interesting fact that this photochemical reaction is sensitive to the presence of a number of widely different substances. Henri and Wurmser[1] found that sulphuric acid, sodium hydroxide, iodine, mercuric chloride, potassium cyanide, sodium thiosulphate, and hydrogen sulphide act as preservatives for hydrogen peroxide with respect to the light decomposition. Our present paper includes acetanilide, sodium chloride, sulphuric acid, calcium hydroxide, sodium hydroxide, and barium hydroxide.

It will be noted that our results with sodium hydroxide and sulphuric acid check those of Henri and Wurmser, qualitatively at least.

All the above substances act as negative catalysts. The case of sodium hydroxide is especially interesting on account of the fact that this substance is a powerful positive catalyst

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[1] Comptes rendus, 157, 284 (1913).

for the heat decomposition of hydrogen peroxide.[1] On the other hand, calcium hydroxide, which has no effect on the heat reaction,[1] shows a marked preservative action with respect to the light reaction.

Our method of studying the effect of catalysts on the photochemical reaction was as follows:

The decomposition of a pure solution of hydrogen peroxide was begun as in our previously described experiments, and the reaction followed by titrating weighed samples from time to time until the rate of the decomposition was definitely ascertained. When the decomposition had proceeded smoothly for two or three hours, a very small known quantity of the catalyst, dissolved in 1 cc of water, was squirted into the peroxide solution near the middle of the reaction tube. The sampling and titrating were then continued until the new rate of decomposition became established.

The addition of the 1 cc of water will, of course, dilute the peroxide solution, so that the first point determined after adding the catalyst, will, in general, lie below the prolongation of the old decomposition curve, if the next titration sample is taken soon after adding the catalyst. The magnitude of the dilution effect will depend upon the strength of the peroxide solution and its volume at the time the catalyst is added, and, in general, will be the greater the higher the concentration of the peroxide. The first point on the new curve may also lie slightly below the new curve itself, as determined by subsequent points, due to an excess local dilution in the neighborhood of the point from which the titration sample is withdrawn. This is more likely to occur when the sample is taken very soon after the addition of the catalyst, before the solution has had time to become uniform. Fig. 6 shows this effect.

If a longer time elapses between the addition of the catalyst and the next sampling, it is obvious that the first point on the new curve will lie above the prolongation of the

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[1] Walton and Judd: Zeit. phys. Chem., 83, 315 (1913).

old curve if the catalyst added acts as a preservative. An example of this sort we see in Fig. 4, where the interval was about 36 minutes.

That the effect we have called a dilution effect, was in reality due to dilution alone, and that the dilution had no effect on the rate of decomposition, was experimentally verified by making a run with the addition of pure water instead of a solution of catalyst. Curves I and II of Fig. 9 show the result.

It will be noted in each case that the peroxide solution at the time of adding the catalyst was of such a strength that the decomposition curve would not have differed essentially from a straight line for many hours. The change in direction of the curve cannot, therefore, in any case be ascribed to the normal change for a logarithmic function, as shown, for example in Figs. 2 and 3, where the concentrations were quite small.

While hydrogen peroxide is undoubtedly *formed* by the action of light on water,[1] this factor does not enter into our experiments. In the first place, the amount of peroxide formed, even under the most favorable condition, is small compared with the changes of concentration which we are measuring; and furthermore, Tian[2] has shown that the formation of hydrogen peroxide in water is accomplished only by the extreme ultraviolet, in the neighborhood of 190 $\mu\mu$. While uviol-glass is much more transparent to the shorter wave lengths of light than is ordinary glass, its lower limit of transparency is at about 250 $\mu\mu$, and it would therefore cut off the rays which are effective in the *formation* of hydrogen peroxide.

Effect of Sulphuric Acid

Sulphuric acid exerts a marked preservative action on the photolysis of hydrogen peroxide, a fact which Henri and Wurmser have already noted. In Fig. 4, Curve I represents

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[1] Thiele: Zeit. angew. Chem., **22**, 2472; Ber. chem. Ges. Berlin, **40**, 4914 (1907); Kernbaum: Comptes rendus, **149**, 273 (1909); Tian: Ibid., **152**, 1012 (1911).

[2] Tian: Comptes rendus, **152**, 1483 (1911).

the rate of decomposition before, and Curve II the rate after, the addition of the acid. The acid was of such a strength as to make the whole solution 0.07 percent or *N*/70 H_2SO_4.

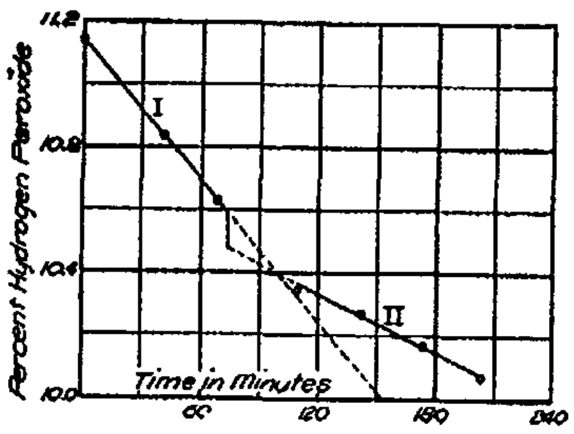

Fig. 4

Effect of Sodium Chloride

Five hundredths of a percent of sodium chloride has a marked preservative influence with respect to the light reaction. In Fig. 5, Curve I represents the rate of decomposition without the catalyst, and Curve II the rate after adding the salt.

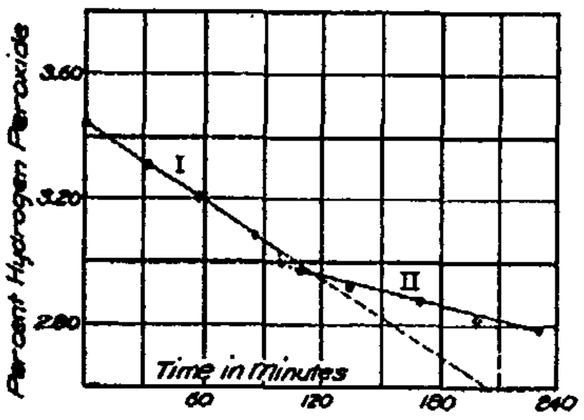

Fig. 5

Effect of Acetanilide

Four hundredths of a percent of acetanilide (the amount contained in Eimer & Amend's 3 percent peroxide) stops the light reaction abruptly, as Fig. 6 shows.

An acetanilide solution of only 0.0008 percent exerts a marked preservative action.

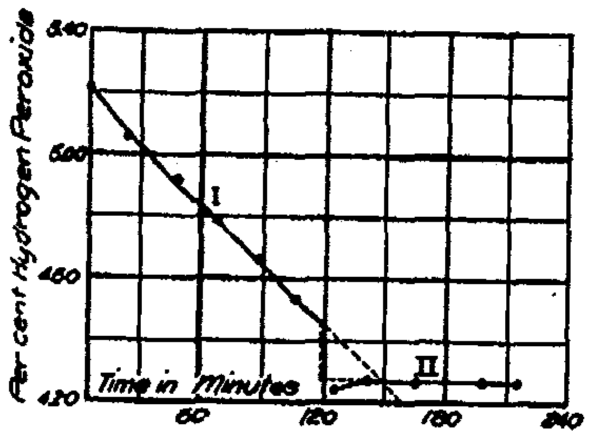

Fig. 6

Effect of Calcium Hydroxide

The preservative effect of calcium hydroxide is shown in Fig. 7. The strength of the lime-water added was such as to make the whole solution 0.002 percent or about $N/1850$.

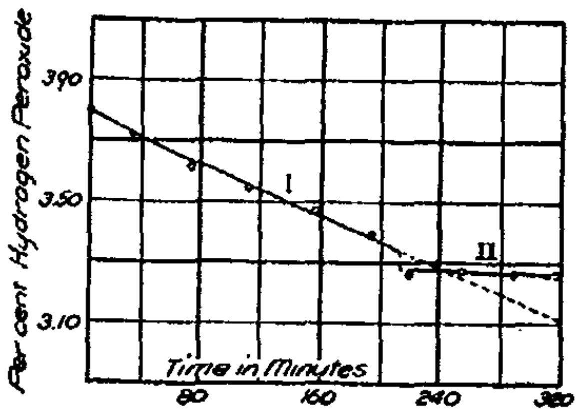

Fig. 7

Effect of Sodium Hydroxide

Fig. 8 shows the effect of adding sodium hydroxide to give a 0.053 percent or about $N/75.5$ solution.

Henri and Wurmser have noted this effect.

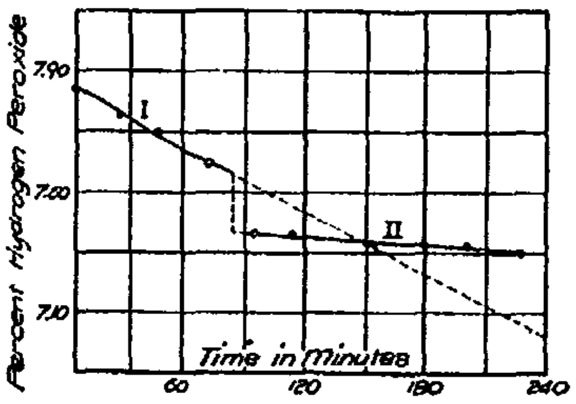

Fig. 8

Effect of Barium Hydroxide

Barium hydroxide, as does calcium hydroxide, acts as a preservative. In Fig. 9, Curves I and II show the effect of adding 1 cc of pure water, while Curves II and III show the effect of adding 1 cc of baryta water. Strength of baryta solution, after mixing with peroxide solution, 0.007 percent or approximately *N*/1220.

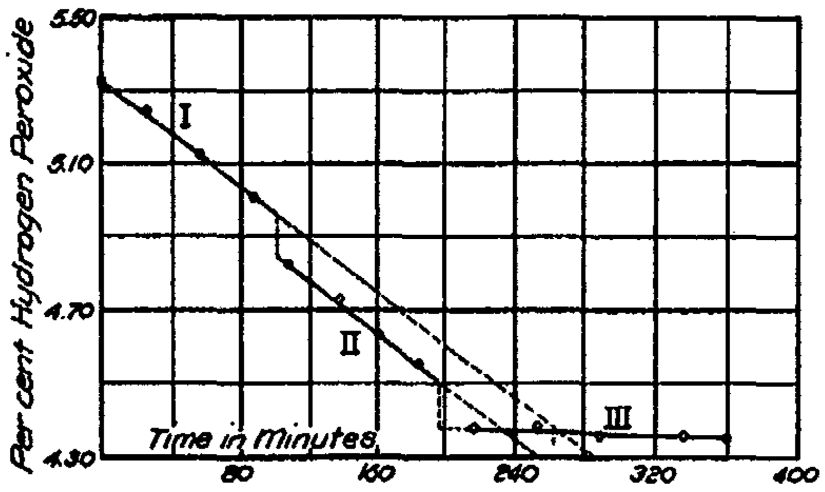

Fig. 9

All of the experiments on the effect of catalysts were carried out at 25°. It will be noted that differences in concentration are plotted on a large scale, so that very small variations, due, in part, at least, to experimental errors, are magnified. For example, in Fig. 7, where the points do not line up very well, the maximum variation from the curve is less than 0.025 percent H_2O_2.

Summary

1. We have described an apparatus suitable for studying certain photochemical reactions, and have applied it to the decomposition of hydrogen peroxide by light (Fig. 1).

2. The photolysis of hydrogen peroxide proceeds smoothly, at constant temperature and illumination following the course of a unimolecular reaction (Fig. 3 and Table I). The reaction ceases abruptly upon extinguishing the light, *i. e.*, it is a pure photolysis and not a secondary reaction, as is the case when blood serum salts are present (Fig. 2).

3. The temperature coefficient of the light reaction is approximately 1.5 (Tables II, III, IV, V).

4. The following substances act as negative catalysts for the light reaction:

Sulphuric acid, *N*/70, Fig. 4.
Sodium chloride, *N*/116, Fig. 5.
Acetanilide, 0.04 percent, Fig. 6.
Lime-water, *N*/1850, Fig. 7.
Sodium hydroxide, *N*/75.5, Fig. 8.
Baryta-water, *N*/1220, Fig. 9.

Laboratory of Physical Chemistry
University of Wisconsin
Madison, Wisconsin
November, 1913

NEW BOOKS

Liquid Air, Oxygen and Nitrogen. *By Georges Claude. Translated by H. E. P. Cottrell. 26 × 18 cm; pp. v + 418. Philadelphia: P. Blakiston's Son & Co., 1913. Price: $5.50.*—In the foreword the translator says:

"Great as is the present importance of the manufacturing processes connected with the production of liquid air, oxygen, and nitrogen, there can be no doubt that it will increase immeasurably in the future, for the known applications of these processes, though already numerous, will not be a tithe of those which cannot fail to be progressively discovered and placed at the disposal of civilization. This reason, even if no other existed, would have afforded a sufficient inducement for providing a standard work on this subject in the English tongue, an acknowledged want which the present translation, it is hoped, will help to satisfy.

"The problem of supplying the ever-increasing demand for nitrogen, in forms suited to agriculture, is a pressing one, to which the relatively excessive cost of nitrogenous manures bears eloquent testimony. Many of the keenest minds of the chemical world have, for the last fourteen years, been devoting themselves to the solution, which ultimately implies recourse to the practically inexhaustible stores of atmospheric nitrogen in a more or less direct fashion. This in turn implies the solution of the problem of the separation of the air into its constituent elements; and the method of distillation and rectification at very low temperatures, on which both Linde's and Claude's processes are based, has been, up till now, the most favored because of the very high degree of purity with which the nitrogen so distilled from the air is produced.

"The day of nitrogen derived from the air has definitely dawned, and manufactures of its products and derivatives on a grand scale are springing up all over the world, so that within a comparatively short time the old sources of supply of ammonia and nitrates will no longer be the chief and practically only sources on which agriculture can depend for replenishing the ever-depleting stores of nitrogen in the soil. Had the means of producing and distilling liquid air not been developed when they were, as described in the following volume, the day when chemical manufactures shall have rendered the nitrogen famine, predicted by Sir William Crookes, impossible, would unquestionably have been still in the dim future instead of well in sight and rapidly approaching."

The first part of the book is devoted to the liquefaction of gases, the second part to the commercial liquefaction of air, the third to the preservation and properties of air, and the fourth to the separation of air into its elements. The subject matter in regard to commercial liquefaction is treated under the headings: expansion and Siemens' exchange of temperature—from Siemens to Linde; the imperfections of the gaseous state and the work of van der Waals; expansion by simple outflow; expansion with external work that can be recuperated. Under the separation of air into its elements, the headings are: general considerations—diverse processes; particulars of the evaporation of liquid air; the recuperation of cold; various processes for progressive evaporation; the accelerated liquefaction of the oxygen of the air; some considerations on the liquefaction of gaseous mixtures; application of the antecedent liquefaction of the oxygen of the air; rectification; grouping of apparatus—existing plants.

The author and Linde are the two men who have done the most work on the commercial liquefaction of air, so the subject is treated by an acknowledged authority. The book is written in the vivacious style which is so difficult to reproduce successfully in English. The translator has been handicapped by the fact that certain French idioms, p. 277, become double negatives when translated too literally. It is a matter of opinion whether the book might not have been improved either by making it more popular or more technical; but it is both readable and valuable in its present form. *Wilder D. Bancroft*

Die Atomionen chemischer Elemente und ihre Kanalstrahlen-Spektra. *By J. Stark. 22 × 15 cm; pp. 47. Berlin: Julius Springer, 1913. Price: 1.60 marks.*—In these few pages the author gives a welcome outline of the recent work on canal ray spectra. This is of great importance because it gives us a direct method of determining the equivalent weights of all the positive ions that are to be found in the gas under study. From our knowledge of the chemical composition, it is comparatively simple to determine the molecular weights and valences of the ions in question. In consequence, we now speak freely of univalent, bivalent, and trivalent, monatomic ions of mercury, aluminum, nitrogen, oxygen, sulphur, chlorine, iodine, and argon. With boron, magnesium, carbon, silicon, and helium, the trivalent monatomic ions have not been discovered but we may live in hope. The red spectrum of argon is now attributed to the univalent ions, and the blue spectrum chiefly to the bivalent ions. The electrolytic ion differs from the gaseous ion by being swaddled in adsorbed water, which masks the absorption spectrum. *Wilder D. Bancroft*

Der kolloide Schwefel. *By Sven Oden. 29 × 22 cm; pp. 193. Upsala: Akademische Buchhandlung, 1913. Price: 10 kronen.*—This is an admirable monograph, dealing as it does with the preparation, purification, properties, and changes of colloidal sulphur. One of the very interesting points is that sulphur is precipitated reversibly by potassium salts, whereas precipitation is irreversible in case a barium salt is added at a moderate concentration and is allowed to stand in contact with the precipitated sulphur for some time. Irreversible precipitation can also occur with sodium chloride at 80°. The theory is quite simple after somebody else has pointed it out. Precipitation is reversible in case one washes out the precipitating agent before agglomeration has taken place. Agglomeration takes place more readily when there is a large percentage excess of coagulating agent or when the temperature is raised. If a high concentration of a coagulating agent is necessary to cause precipitation, it will be relatively easy to wash the adsorbed precipitating agent out of the precipitate, whereas this will be practically impossible if the precipitating agent acts in very dilute solutions. With a solution like barium chloride, a dilute solution of which precipitates sulphur, it is very easy to have a large percentage excess and therefore the precipitation becomes irreversible very much more rapidly than when sodium chloride is the coagulating agent. It seems probable that we shall find the same relations for all our suspension colloids, in which case the arbitrary and inaccurate distinction of an essentially irreversible precipitation will disappear. The value of this monograph is therefore far-reaching.

The author considers that colloidal sulphur is essentially insoluble sulphur. It should therefore be possible, theoretically, to prepare colloidal solutions of rhombic and of monoclinic sulphur; but this has not been tried. No reference is made to the fact that Raffo's colloidal sulphur is very sensitive to potassium sulphate and not sensitive to sodium sulphate. *Wilder D. Bancroft*

Gas Analysis. *By L. M. Dennis. 19 × 13; pp. v + 434. New York: The Macmillan Co., 1913. Price: $2.10.*—In the preface the author states that, "In general plan this book follows the last edition of the English translation of Hempel's 'Methods of Gas Analysis.' It was indeed begun with the intention of having it serve as a new edition of that work, but the many advances in the field of gas analysis during the last fourteen years have necessitated the incorporation of much new material and the modifications or excision of many of the older methods. In view of this fact, a new book has been written." On comparing the two books, it can be seen that about 45 percent of the subject matter is new, about 30 percent copied directly from the English translation of Hempel's book, and about 25 percent rewritten. Where the material is copied, no reference is given to the original work, although a goodly number of references are given throughout the book to a large number of sources from which less material is taken. About 50 percent of the drawings for the cuts are new. The remainder of the cuts are taken from the translation of Hempel's book. The new cuts are an improvement over the old ones, but the draftsman has used too much shading. A number of the drawings appear to have "skin disease.". In a number of the cuts, the apparatus is assembled so that too much unnecessary space is taken up.

The book, however, as a whole, is better than the translation of Hempel's original work. It is written up and arranged in better form. The paragraphs have headings printed in heavy type, so that it is easier to find what one wants. It is gratifying to see the Friedrichs' spiral washing bottle, and tube, given such an important place. They can be relied upon to give satisfaction for rapid absorption, and efficient washing of gases. The modifications of the Orsat apparatus and the Petterson-Palmquist apparatus, are important. The size of the apparatus has been markedly decreased. The introduction of the Friedrichs' spiral washing or absorption tubes in the Orsat increases the efficiency and the rapidity of the absorption. The capillary dead space is very much decreased. The reagents are also better protected from the air.

The advantages of a number of the suggested forms of apparatus are of questionable value, however. The Pannertz apparatus for specific gravity does away with the inconveniences of operation of the Schilling apparatus, but only at the expense of accurateness. The gas will be subject to the temperature fluctuations of the air, the apparatus not being surrounded with water. Also, probably the most important objections to this apparatus is the possibility of getting water in the capillary at the top. For practical work, the Schilling apparatus is unquestionably the better of the two on account of its "foolproofness."

Another piece of apparatus suggested is a portable form of the Hempel apparatus. From the description of this, the apparatus is of questionable value. The length of the whole apparatus, Fig. 40, is given as 20.5 cm. It can be seen that the burette, where the graduations must appear, is only 15 cm long. The burette holds 50 cc. By calculation it is seen that the internal diameter of the burette must be 2 cm. One centimeter length of the burette must correspond to 3 cubic centimeters of the gas. Calibrated in fifths, the scale would almost resemble a "diffraction grating." The accuracy would not be greater than one-third that of the ordinary apparatus.

The suggested use of ammoniacal chloride for absorbing carbon monoxide is of doubtful value. From experiences of the reviewer with furnace gases containing carbon monoxide, the hydrochloric acid solution of cuprous chloride gives much better satisfaction. The chapter on combustion of gases is rather vague. It is interesting to note, p. 131, that hydrogen is a hydro-carbon.

It is true that oxygen 50 percent pure can be absorbed quietly by phosphorus but the sticks of the absorbent will melt if the percentage oxygen be greater than about 30 percent.

It is a pity to recommend exposing a gas mixture to daylight, and waiting for 12 hours, to eliminate ozone, when the oxyhydrogen gas may be generated free from impurities if barium hydroxide be used as electrolyte instead of sulphuric acid.

The modification of the Hempel nitrometer cannot be recommended for practical work. There are too many breakable parts. Works interested in the use of the nitrometer, generally have simple modifications to suit their specific needs, so that there will probably be no wide application of the more complex apparatus.

Attention may be called to useful additions in a number of cases. The gas volumeter, and baroscope; apparatus for distillation of mercury; automatic apparatus in flue gas analysis, Junker's Calorimeter, and the whirling Psychrometer, bring the book up to date.

The book is hard reading, on account of the intimate mixture of general discussion and extremely specific instructions as to manipulation. The style partakes too much of the "turn stopcock *a*" variety. The directions for manipulation might be put in smaller print. This would not sacrifice the unity, but would make it easier for the analyst, as well as the general reader, to find the desired information. A number of small errors should be corrected in the next edition. *C. W. Bennett*

General Chemistry. *By J. C. Blake 20 × 14 cm; pp. v + 417. New York: The Macmillan Company, 1913. Price: $1.90 net.*—In the preface the author says:

"The order of presentation of the subject matter differs in so many particulars from that of any previously published text which has come to my notice that a full discussion or attempt at 'justification' of all such deviations seems futile..... Some brief account of the secondary principles which have helped to determine the sequence of the work may, perhaps, not be out of place. The main chemical thread which runs throughout the work is that of chemical potential. This statement needs no further explanation, as all chemists will know that the book represents, therefore, an interpretation of the 'new' chemistry rather than the 'old.' The method of approach, however, is to a certain extent unique, based as it is on the data of thermochemistry....Perhaps the next most important principle which has determined the order of presentations, as well as the nature of much of the information conveyed, is Mendeléeff's Law as expressed in the extended periodic arrangement of the elements. This arrangement, as contrasted to the condensed arrangement, represents continuity in the chemical and physical properties of the elements from one end of a long series to to the other . . . . . Next in importance is the principle of oxidation and reduction and the closely associated problem of the chemistry of hydrogen. The treatment of the latter subject alone approaches the polemic, because the condition of the literature of the day seems to demand it . . . . . The ionic theory in particular has not been introduced in a controversial manner. The law of mass action, on the other hand, has not been emphasized from its quantitative aspects. Various other laws of physical chemistry have been used rather than proved.

"The position assigned to 'Organic Chemistry' and to 'Applied Chemistry' has been justified by experience. Even this much (or little) organic chemistry seems wholly out of place in connection with the inorganic chemistry of carbon; whereas the introduction of simple tests of real value (as it is thought) to the student whose chemistry ends with this course meets with enthusiastic and universal favor with the students. I have pitted this work against the tedious descriptions of industrial processes usually found in 'modern' text-books, especially those of high school grade, which in my opinion can be of living interest only to the chemical or industrial engineer."

The subject matter is treated under four heads hydrogen and the acid-forming elements; the base-forming elements and the elements without chemistry; organic chemistry; applied chemistry. The book is "written primarily for the use of the great majority of college students whose formal study of chemistry last only one year." On p. 166 there is the interesting definition that "molecules are the homogeneous particles into which a liquid or solid substance disintegrates when it passes into the gaseous state or into (true) solution." The reviewer does not agree with paragraph on p. 191. "The stage of oxidation represented by lead oxide is about the only one requiring any further attention, as it is the only one which gives any common salts. For this reason it is usually spoken of as lead oxide simply, and its salts as the lead salts. Thus $PbCl_2$ is called lead chloride and not plumbus or plumbic chloride. Indeed it would be wrong to name it either of these: to make it plumbous chloride would be to imply that $PbCl_4$ is plumbic chloride whereas it is merely a chemical curiosity, called lead tetrachloride (compare $SiCl_4$); to name it plumbic chloride would imply that there is a plumbous chloride, whereas, in reality, while there may be a suboxide of lead, having the formula Pb_2O, yet it gives rise to no (plumbous) salts and is seldom called plumbous oxide." *Wilder D. Bancroft*

Outlines of Theoretical Chemistry. *By Frederick H. Getman. 21 × 15 cm; pp. vii + 467. New York: John Wiley & Sons, 1913. Price: $3.50 net.*—In the preface it is stated that:

"The present book is designed to meet the requirements of classes beginning the study of theoretical and physical chemistry . . . . . Contributions to our knowledge in the domain of physical chemistry have increased with such rapidity within recent years that the prospective author of a general text-book finds himself confronted with the vexing problem of what to omit rather than what to include . . . . . The attempt has been made to present the more difficult portions of the subject, such as the osmotic theory of solutions, the laws of equilibrium, and chemical action, and the principles of electrochemistry in a clear and logical manner."

The book, then takes up fundamental principles; the electron theory; consideration of gases, liquids, and solids; solutions; thermochemistry; chemical statics and dynamics; electrochemistry; and actinochemistry. The treatment is approximately the same as that of the standard works. There is not much unity in this treatment. No chapter seems to follow from any other. The whole thing seems to be written up as a series of separate departments or chapters. The work is a disappointment in that it has failed to present the reviewer's idea of what is needed in a physical chemistry. It is brief. If any criticism is made it would be that the treatment is too brief. No system appears upon which the treatment is founded, the reviewer's idea being that some connection should be shown between one chapter and another, or the arrangement should be such that the work would be incomplete without every part of the book. This certainly is not shown here. The book contains some things that other physical chemistries do not have, but on the other hand, it omits certain other important phases of the subject. It is not as good as some other books which have been written on the subject. There seem, therefore, to be very few reasons for the appearance of this book. *C. W. Bennett*

Cyanamid. *By Edward J. Franke. 23 × 16 cm; pp. iii + 112. Easton: The Chemical Publishing Co., 1913. Price: $1.25.*—This book is intended as a review of the present knowledge of cyanamid from a chemical and an agricultural standpoint. It is the purpose of the author to bring a review of the literature on cyanamid to those who do not have library facilities, etc., for looking this up. The use and general method of preparation are considered, although no details of the commercial production are given. Methods of analysis and the effect of storage on the product are considered in some detail. A good portion of the book is taken up with the agricultural phase of the subject, specially with the reaction which is supposed to take place in the soil. The decomposition is supposed to take place in three stages; the calcium cyanamid being first hydrolyzed by the moisture in the soil with the formation of cyanamid. The cyanamid is further hydrolyzed to urea which then goes down to ammonium salts. The velocity of these reactions is greatest when the ratio of the soil solutions to the soil is least; when the surface of the soil exposed to the liquid is therefore greatest. Colloid substances, such as hydrated manganese and iron oxides, and some of the zeolites, are the important agents in the decomposition of cyanamid. This is shown because the soil loses the power of decomposition when the colloids are precipitated. The hydrolysis is not dependent on microörganisms because it is most rapid in solutions where the concentration is great enough to preclude the possibility of life. It goes on also in sterile media. If the media is not sterile, the decomposition goes down to ammonium salts. It is concluded that cyanamid is not toxic to plants unless large amounts are added to the soil. The book is closed with a chapter on mixed fertilizers, where cyanamid of course is an important addition.

The book is a disappointment in that it deals practically completely with theoretical material and gives us very little concerning the practical side of the subject. *C. W. Bennett*

THE PRODUCTION OF DIRECT PHOTOGRAPHIC POSITIVES

BY G. A. PERLEY, T. J. TWOMEY AND H. A. ROBINSON

In a previous article[1] the influence of all the variables involved in the production of direct photographic positives by means of thiocarbamide and a hydroquinone developer has been discussed.

The variables considered in the preliminary study were: time of exposure, temperature of development, size of plate, amount of thiocarbamide, amount of hydroquinone, amount of sodium sulphite, and amount of water. The emulsion upon the plate and the source of illumination were considered as maintained at a constant value.

It was found with the above existing conditions that, after exposing a photographic plate for a certain definite time, a developer of the following concentration gave the best positives at 18° C: 0.0030 gram thiocarbamide, 0.0387 gram hydroquinone, 0.075 gram sodium carbonate, 0.2907 gram sodium sulphite, and 7.8461 grams of water per square inch of plate surface.

The bluish brown color of the positive deposit, the appearance of a yellowish fog by reflected light, and the necessity of a preliminary appearance of a thin negative were the chief sources of dissatisfaction with the above conditions. It seemed that with a more intimate knowledge of the real reactions involved it should be possible to produce direct photographic positives unexcelled even by the common method of production. The data of the previous paper indicated that no single constituent of the above developer could be satisfactorily omitted.

In order to obtain direct photographic positives of excellent merit and a method of easy manipulation the problem resolved itself down to four chief lines of attack:

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[1] Perley and Leighton: Jour. Phys. Chem., 17, 235 (1913).

First, an investigation as to what substances cause the decomposition and resultant color of the positive deposit; second, the substitution of another thiocarbamide compound, or some similar agent, which will not stain the emulsion; third, the elimination of the thin negative, either by a solvent after its production, or by the substitution of some other material for the hydroquinone, carbonate and sulphite, thus preventing its formation; fourth, the production of an emulsion which is not stained by thiocarbamide.

The developers used in this work were made up with great accuracy. All solutions were measured from burettes into a crystallizing dish, which served as a developing tray. A developer was used for only one experiment. The following standard solutions were employed:

Hydroquinone	21 grams per liter.
Ortol	30 grams per liter.
Pyrogallol	12 grams per liter.
Metol	35 grams per liter.
Amidol	2.4 grams per liter.
Eikonogen	40 grams per liter.
Sodium carbonate (anhyd.)	16 grams per liter.
Sodium sulphite (anhyd.)	126 grams per liter.
All thiocarbamides	2 grams per liter.

In several of the experiments double strength carbonate and sulphite solutions were used in order to maintain a constant water content. All of the thiocarbamides were prepared and purified by us in the usual manner.

Intimate and careful observations led to the belief that the thiocarbamide must act in some manner as a better solvent for the unexposed silver halide complex than for the exposed portion, and that in the presence of some one, or all, of the constituents of the developer, silver was produced upon the unexposed portions. Just so long as there are hydroquinone, carbonate, and sulphite present in the developer, with a sufficient exposure, a negative must result. The strength of the negative naturally depends upon the degree of exposure. The method from the standpoint of exposure must necessarily have an upper and lower limit of usefulness. The lower must occur when too small an exposure is given to yield a thin negative with the hydroquinone present, in other words, where such an excess of unexposed silver halide is present that the solvent action appears to be uniform over the whole plate. The upper limit must exist at that point where an excessive exposure produces so much exposed silver halide that there is a dense negative masking the silver deposit of the positive portion. Our previously published data verify this.

Since a hydroquinone developer tends to yield a harsh negative, it seemed possible to substitute other "reducers" such as metol, pyrogallol, ortol, amidol, eikonogen, etc., and possibly produce an extremely thin negative which would be especially weak in the high lights. It also seemed probable that the "reducer" might have a more or less greater influence upon the rapidity of reduction of the silver which formed the positive image. If such a condition existed it would be obtained only by a systematic control.

The data of the first paper were obtained under a so-called constant source of illumination. A mercury vapor lamp had been utilized in much of the present work until an error was discovered. The voltage fluctuated a great deal, with the result that the various exposures were far from constant. It seemed wise to establish a new standard of illumination. A wooden box with a sliding front was constructed, of the following dimensions: 22.5 inches long; 9 inches wide; and 13.5 inches high. The interior of the box was painted black to prevent any possible reflection of light. A 15 C. P. 6 volt tungsten lamp was fastened on the interior of the box. The lamp was connected to the storage cells through a resistance and all exposures were made at a constant voltage of 2.5. A lantern slide plate of average density was used as a standard view, and this was located 18.5 inches from the bulb of the tungsten lamp. All exposures were made by the aid of a switch connecting the light to the storage batteries, and a stop watch was used to ensure accurate timing.

Almost an infinite number of experiments were made before the adoption of what seemed the very best possible positive. A tabulation of the vast amount of data would serve no real purpose and accordingly only the final results will be given. It might be interesting to note that the results were obtained only after several thousand individual experiments upon strips of lantern slide plates of a surface area of 4.3 square inches. All of the data were also obtained with a constant exposure of 8 seconds. The present arrangement of the tables was only made possible after it was learned that thiocarbamide and carbonate were alone essential to the formation of the positive image. The discussion of this particular phase comes more logically after a consideration of the influence of the various "reducing" agents.

The Imperial Special lantern slide plates were always employed in the work, and the temperature was maintained at 20–21° C.

The data given in Table I represent those as obtained by us for the production of the best positive by means of thiocarbamide and various "reducers." The results are expressed in units per square inch of plate surface. The figures do not represent the minimum quantities of the constituents of the developer essential for the production of a positive. The tables show the relative concentration of the constituents which gave the very best results. It was found that if it was desired to produce a full size lantern slide (3.25 × 4) it was only necessary to increase each of the constituents ten times that given in the table. Such a developer will yield only one first-class positive.

It seemed advisable to maintain the amounts of water in each experiment at a constant value. The effect of sulphite is such that it may be varied between fairly wide limits, and for the sake of comparison, this constituent of the developer was maintained at a constant amount.

TABLE I

Exposure in seconds	8
Voltage across tungsten lamp	2.5
Time of development	2–2$^1/_2$ minutes
Temperature	20–21° C
Sodium sulphite	0.234 gram per square inch of surface
Water	9.3 grams per square inch of surface

Concentrations of constituents expressed in grams per square inch of plate surface.

	Reducer	Thiocarbamide	Sodium carbonate	Color of positive
Hydroquinone	0.034	0.0009	0.037	Sepia
Ortol	0.041	0.0030	0.067	Blue-black
Pyrogallol	0.022	0.0032	0.089	Deeper blue-black
Metol	0.032	0.0011	0.205	Dark brown
Amidol	0.004	.0013	0.030	Black with pink stain
Eikonogen	0.074	0.0027	0.100	Blue-black

These data gave us a much better insight into the production of positives. It would be impossible to tabulate all of the important features, so a brief résumé of the results can best be considered.

As far as ease of manipulation is concerned, hydroquinone, ortol, or metol gave results of medium control. Amidol consistently gave excellent positives, but they were covered with a very disagreeable pink stain. This renders the resultant positive useless for either a lantern slide or a transparency. Eikonogen gives too uniform a deposit in the shadows with a flat positive resulting. Occasionally pyrogallol would give a deposit of fair merit, yet the manipulation involved is disagreeable and tiring.

Of the six "reducing" agents examined it would seem that either metol or hydroquinone is best adapted to the process. The chief differences between the various "reducers" could be classified under staining power, color of deposit, and ease of manipulation.

There were some features which were common to the six systems. In each case a small increase in the amount of thiocarbamide caused a rapid fogging of the plate, while a decrease in the concentration of thiocarbamide always yielded positives badly masked in the high lights by a thin negative. An increase in the concentration of carbonate always led to the production of a very dense blue positive with an excessive amount of negative in the high lights. A decrease in carbonate yielded anything from yellow and red stained positives to a thin negative. It was very interesting to note that, commencing with an excess of carbonate, a continued decrease of this substance in any series always caused the resultant color effect to pass through the yellowish brown, to the yellow, and then to pink and red. A very meager examination of these plates would indicate that there is a wide difference in the size of the particles. The red deposits were so small that an ordinary laboratory microscope was useless in the examination, while the blue deposits could be observed with ease.

Too small a quantity of the "reducers" yielded fogged plates, while an excess always gave for the most part a negative. The sulphite in each case could be varied through a much wider range than the other constituents. Too small or too large amounts always resulted in the production of positives masked in the high lights with a negative.

When the quantity of water was too small, or in other words, when the total concentration was increased, a negative resulted. With too great dilution a fogged plate was obtained. The effect of temperature seemed to be very nearly the same in all cases. Too low a temperature of development always retarded the formation of the positive, with a negative as the result, while an excessive temperature produced a badly fogged plate.

It would thus seem as if the rôle of the "reducer" was chiefly in the slight reduction of the latent image, and that the formation of the positive was independent of any one particular type of "reducer." It is most certain that the presence of the "reducer" has some effect upon the color of the positive deposit, yet this influence might be one due to the nature of the medium.

Since the previous study had led us to believe that one of the essentials for the production of positives was the presence of some solvent for the unexposed silver halide complex, it seemed important to study the effect of various substituted thiocarbamides. A long series of experiments were conducted very similar to those which led to the acceptance of the data presented in Table I, with the exception that allyl thiocarbamide was substituted for the simple thiocarbamide. Again a very interesting set of results was obtained. The best data are presented in Table II.

TABLE II

Exposure in seconds	8	
Voltage across tungsten lamp	2.5	
Time of development	$2–2^{1}/_{2}$	minutes
Temperature	20–21° C	
Sodium sulphite	0.234	grams per square inch of surface
Water	9.3	grams per square inch of surface

Concentration of constituents expressed in grams per square inch of plate surface.

	Reducer	Allyl thiocarbamide	Sodium carbonate	Color of deposit
Hydroquinone	0.034	0.0014	0.011	Red
Ortol	0.041	0.0018	0.042	Purple-brown
Pyrogallol	0.022	0.0023	0.033	Yellow with stain
Metol	0.032	0.0037	0.052	Reddish brown
Amidol	.004	0.0027	0.022	Blue-black with stain
Eikonogen	0.074	0.0055	0.052	Bluish purple

Not only was it evident that the "reducer" has a great influence upon the color of the positive deposit, but it was equally true that the thiocarbamide compound was of still greater importance.

From the viewpoint of ease of manipulation, it can be stated that after using allyl thiocarbamide any one familiar with the control of the simple thiocarbamide would forever dread to return to the use of the simple salt. A much wider range of variation of the constituents of the developer was afforded with the use of allyl thiocarbamide than with the simple substance. An extremely slight variation of the concentration of thiocarbamide was always sure to yield an exceedingly poor positive, irrespective of the type of "reducer." In every case where the allyl compound was used it gave far superior control to the corresponding thiocarbamide results of Table I.

The observation had been made in a few cases of Table I that the positive deposit altered in color as it dried. In Table II this fact became more evident. After washing the plate from the development with allyl thiocarbamide and hydroquinone and fixing, the color of the deposit was somewhat of a yellowish brown. When dried the deposit was red. In the case of allyl thiocarbamide and metol the deposit was deep red when wet, and it dried to a reddish brown. With allyl thiocarbamide and eikonogen the wet deposit was nearly black, while it dried to a most beautiful bluish purple. This color change was practically always the same, whether a rapid or a slow drying was utilized, or whether the plate dried in the dark or in bright light.

Another manipulative difference between the simple substance and the allyl thiocarbamide was in the susceptibility to surface stains. With thiocarbamide an uneven immersion in the developer, or a failure to keep the developer in constant motion, always resulted in spotted and irregular stains. This particular feature seemed to be practically absent in the work which resulted in the data of Table II. In either table the emulsion side of the plate could not be handled with moist fingers before or after exposing without the fact being in great evidence.

As in the data of Table I we found the control of the pyrogallol and allyl thiocarbamide developer rather unpleasant. It was interesting to note that every possible combination yielded yellow stained plates. The use of amidol and allyl thiocarbamide produced stained inferior plates.

The use of allyl thiocarbamide with either hydroquinone, metol, or eikonogen was nearly all that could be desired. There was but little danger of the masking negative which was so much in evidence with the working of the simple substance.

The direct production of transparencies of a red color or of a bluish purple can be controlled most readily by the use of either the hydroquinone, or the eikonogen and allyl thiocarbamide developer as given in Table II.

Again, as in Table I, we found many features in common to all of the systems thus far studied. The effect of an excess or too small quantity of the "reducer," sodium carbonate, sodium sulphite, the thiocarbamide compound, or water was perfectly analogous to that observed and given in the previous consideration of Table I. As has been noted, there was a greater opportunity for variation of the constituents in the use of allyl thiocarbamide developers, yet an excessive variation gave the same final results as in the systems of Table I.

Since the influence of the allyl thiocarbamide had been a factor towards improvement, it seemed of interest to learn something concerning the effect of the ethyl compound. Another endless series of experiments similar to those which led to the data of Tables I and II was undertaken. The best final data are given in Table III.

TABLE III

Exposure in seconds	8	
Voltage across tungsten lamp	2.5	
Time of development	2–2$\frac{1}{2}$	minutes
Temperature	20–21° C	
Sodium sulphite	0.234	gram per square inch of surface
Water	9.3	grams per square inch of surface

Concentration of constituents expressed in grams per square inch of plate surface.

	Reducer	Ethyl thiocarbamide	Sodium carbonate	Color of deposit
Hydroquinone	0.034	0.0116	0.037	Reddish purple
Ortol	0.041	0.0116	0.077	Blue-brown
Pyrogallol	0.022	0.0069	0.100	Red with red stain
Metol	0.032	0.0037	0.100	Red
Amidol	0.004	0.0046	0.033	Blue-black with pink stain
Eikonogen	0.074	0.0069	0.026	Blue

The use of ethyl thiocarbamide in the production of direct photographic positives is exceedingly similar to that of the allyl compound. Hydroquinone, metol, and eikonogen developers work exceedingly well. The ethyl compound permits even greater range of variation than the allyl thiocarbamide. Amidol gives badly stained plates, while pyrogallol gives a beautiful positive deposit of a red color, yet a red stain makes it almost useless. Ortol gives a positive of fair quality. The metol-ethyl thiocarbamide developer of Table III gives exceedingly fine positives. With this particular developer only a mere trace of a negative is produced, and the masking action is negligible. The differences between the action of ethyl thiocarbamide and thiocarbamide are practically the same as those between allyl thiocarbamide and the simple substance. Since the same description applies to this series as to that of Table II, it seems unnecessary to repeat it in full.

The important facts dealing with the data of Table III are that the ethyl thiocarbamide yields a positive deposit of different colors from either of the corresponding series with thiocarbamide and allyl thiocarbamide. The data on the influence of the other constituents of the developers are perfectly analogous to that of the thiocarbamide and the allyl compound. The manipulation is far easier than that of the thiocarbamide developer. The colors of some of the positive deposits altered during drying.

It seemed advisable to make another series using tetra thiocarbamide ammonium bromide in place of the thiocarbamide. Frary[1] has suggested the usefulness of this developer under the right conditions. The best data are given in Table IV.

TABLE IV

Exposure in seconds	8
Voltage across tungsten lamp	2.5
Time of development	2–$2^1/_2$ minutes
Temperature	20–21° C
Sodium sulphite	0.234 gram per square inch of surface
Water	9.3 grams per square inch of surface

Concentration of constituents expressed in grams per square inch of plate surface.

	Reducer	Tetra thio-ammonium bromide	Sodium sulphite	Color of deposit
Hydroquinone	0.034	0.0011	0.30	Sepia-brown
Ortol	0.041	0.0054	0.078	Yellowish brown
Pyrogallol	0.022	0.0046	0.068	Blue
Metol	0.032	0.0032	0.205	Blue-black
Amidol	0.004	0.0018	0.033	Black with pink stain
Eikonogen	0.074	0.0012	0.089	Blue-black

The data of Table IV represents the results of a great many experiments. The tetra thiocarbamide ammonium bromide bears an exceedingly close analogy to the simple thiocarbamide. With but few exceptions the colors for the best of each member of the series as given in Table IV were decidedly similar to those given in Table I. This compound is fully as difficult to manipulate as the simple salt. In view of the results obtained with the allyl and ethyl compounds, the bad features of the tetra thiocarbamide ammonium bromide

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[1] Frary: Jour. Phys. Chem., 17, 33 (1913).

developers would not give it application in the production of transparencies.

The same results were obtained with this compound as with the thiocarbamide under the influence of varying concentrations of the other constituents of the developer. Hydroquinone and metol gave the most readily controlled results. The deposit with amidol was of fair quality and the best of any of the amidol series. The pink stain is the drawback.

There are twenty-four different types of developers considered in the first four tables of this article, and each developer is capable of giving a positive of a more or less good quality under the conditions as outlined. There is a very wide range of colors in the resultant positives. The reds and blues predominate. It is interesting to note that all of the hydroquinone series gave sepia-brown to red coloration, all of the eikonogen series gave some shade of blue, the ortol series gave colors ranging from yellowish brown to a bluish black, the amidol deposits were chiefly black, covered with a pink stain, while pyrogallol yielded all sorts of colors from red, through the yellows, to a blue.

In all cases the influence of the "reducer" upon the formation of the positive seemed to be the same. The function of the thiocarbamide is an important one, while the influence of the carbonate is nearly as great.

All of our data pointed to the fact that the chief rôles of the "reducer" and sodium sulphite were in developing the latent image. In all cases the formation of the final positive passed through the same stages. After a few seconds development, a thin negative always seemed to appear; this came, on an average, after 15–20 seconds immersion; after this, the plate passed through a stage of thin fogging, and then came the building up of the positive deposit; the commencement of the formation of the positive is between 45 seconds and 1¼ minutes after immersion.

The allyl thiocarbamide-hydroquinone and the allyl thiocarbamide-eikonogen developers of Table II, the ethyl thiocarbamide-metol and the ethyl thiocarbamide-eikonogen developers of Table III showed but minimum traces of a negative during the development. In the case of the ethyl thiocarbamide-metol developer of Table III, it seemed as if the positive image was the only one to develop. These four types of developers would seem to be applicable to the production of blue or red transparencies with good success.

The effect of sodium sulphite seemed to be dependent upon the type of "reducer" employed. In any of the series of the previous four tables it is possible to obtain positives in the absence of sodium sulphite. In the absence of sodium sulphite, an entirely different ratio of carbonate to the thiocarbamide must be employed in order to obtain a positive. The omission of sodium sulphite in the hydroquinone, pyrogallol, and eikonogen series was investigated with greater detail than in the others. With pyrogallol-allyl thiocarbamide and eikonogen-allyl thiocarbamide without sulphite, a very good positive could be obtained of but slightly different color from that in the presence of sulphite. The omission of sulphite in the hydroquinone-allyl thiocarbamide developer yielded a pure black positive with a mottled effect. This positive was a great deal inferior to that obtained in the presence of sulphite. The best concentrations employed are given in Table V.

TABLE V

Exposure in seconds	8
Voltage across tungsten lamp	2.5
Temperature	20–21° C
Sodium sulphite	0
Water	9.3 grams per square inch of surface

Concentrations of constituents expressed in grams per square inch of plate surface.

	Reducer	Allyl thiocarbamide	Sodium carbonate	Positive deposit
Hydroquinone	0.019	0.0014	0.067	Poor, mottled black
Eikonogen	0.074	0.0050	0.071	Good, blue
Pyrogallol	0.022	0.0023	0.055	Good, yellow stained positive

It is quite evident from the data of Table V that in the case of the hydroquinone-allyl thiocarbamide developer the influence of sulphite upon the deposition of the positive image is great. In the other cases the effect is practically negligible.

In the previous paper[1] we had concluded that sodium sulphite was essential for the production of a positive. It will be observed in each case in the absence of sulphite it requires a far greater amount of sodium carbonate than with sulphite present (see Table II for comparison). The reason for our failure to obtain positives in the first paper, in the absence of sulphite, was due to an insufficient quantity of sodium carbonate.

Another series of experiments was made to determine the effect of the addition of varying quantities of sodium sulphite upon the allyl-thiocarbamide-hydroquinone developer of Table V.

The results are given in Table VI.

TABLE VI

Exposure in seconds	8
Voltage across tungsten lamp	2.5
Temperature	20–21° C
Sodium carbonate	0.067 gram per square inch of surface
Water	9.3 grams per square inch of surface

Concentrations of constituents expressed in grams per square inch of plate surface.

Hydroquinone	Allyl thiocarbamide	Sodium sulphite	Result
0.019	0.0014	—	Mottled black positive.
0.019	0.0014	0.117	Negative flashes up, and fogs at once.
0.019	0.0014	0.586	Yellow fogged positive.
0.019	0.0014	1.172	Brown less fogged positive.
0.019	0.0014	1.758	Red purple positive of good quality.

The data of Table VI would indicate that possibly sodium

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[1] Perley and Leighton: Jour. Phys. Chem., 17, 235 (1913).

sulphite has a double rôle in this particular developer. A portion of it aids in the formation of the positive deposit. The variation of color from black, to yellow, and then to red by increasing the amounts, shows that it is an influential medium at least. When present in large amounts it acts as a very efficient restrainer for the positive. From the present available data upon this restraining action depends the success of the beautiful allyl thiocarbamide-hydroquinone developer.

The thiocarbamide compound and the sodium carbonate seemed to be the important factors in the formation of the positive. A very close relationship between the concentrations of these two substances seemed ever to be in existence. It was possible to maintain the content of water, "reducer" and sodium sulphite at a constant value and produce positives of good quality with different quantities of carbonate and thiocarbamide. However, unless the definite ratio of carbonate to thiocarbamide as given in the preceding four tables was always maintained, a poor product would result. In other words, with all of the constituents maintained constant, any increase in thiocarbamide over that given in any of the four tables must be accompanied by a corresponding increase of carbonate. Otherwise failure will result.

It seemed wise to determine whether a positive could be produced in the absence of carbonate and the data of Table VII were obtained.

TABLE VII

Exposure in seconds	8
Voltage across tungsten lamp	2.5
Temperature	20–21° C
Sodium carbonate	0
Water	9.3 grams per square inch of surface

Concentrations of constituents expressed in grams per square inch of plate surface.

	Reducer	Allyl thiocarbamide	Sodium sulphite	Result
Hydroquinone	0.034	0.0014	0.351	Blurred, deep blue positive.
Hydroquinone	0.034	0.0014	0.234	Thin negative.

It was necessary to develop the best plate nearly five times as long as those in which the carbonate was present. The positive was of a very beautiful blue color, and if it were not for the fact that a haze remained over the surface, a fine transparency could be produced by this method. The chief difference in the composition of the developer lies in the concentration of sodium sulphite. It was observed that in the absence of carbonate a much larger quantity of sulphite was required than when carbonate was present (see data of Table II).

From the data of Tables V, VI, and VII the problem became most interesting. Using allyl thiocarbamide and a hydroquinone developer it is possible to obtain positives in the absence of either the sulphite, or the carbonate. When one is absent a much larger amount of the other must be present.

Thus, it seemed quite probable that the alkalinity of the carbonate or sulphite had a great influence upon the action of the thiocarbamides. Using the allyl thiocarbamide-hydroquinone developer of Table II, a solution of sodium hydroxide was substituted for the sodium carbonate, with the best results given in Table VIII.

TABLE VIII

Exposure in seconds	8
Voltage across tungsten lamp	2.5
Time of development	2–$2^1/_2$ minutes
Temperature	20–21° C
Sodium sulphite	0.234 gram per square inch of surface
Water	9.3 grams per square inch of surface.

Concentration of constituents expressed in grams per square inch of plate surface.

Hydroquinone	Allyl thiocarbamide	Sodium hydroxide	Result
0.034	0.0014	0.0026	Excellent positive of purple color.

The positive resulting was one of the best obtained in all of the experiments. It was easily controlled. The influences of the various constituents of the developer were perfectly analogous to the corresponding series of Table II in which carbonate was used. It is to be noted that for a given content of hydroquinone, allyl thiocarbamide and water, in the absence of the other two agents, it requires only a small quantity of sodium hydroxide, a larger amount of sodium carbonate, and a much greater quantity of sodium sulphite to produce positives of good quality. In the first part of this paper it was suggested that thiocarbamide acted as a better solvent for the unexposed silver halide complex than for the exposed portion, and in the presence of some of the constituents of the developer silver was again reduced from the dissolved portion of the complex. Such a theory was not in evidence in the beginning, yet each experiment made a step in advance towards accepting such a conclusion.

Valenta[1] has determined the solubility of the silver halides in some of the thiocarbamides. In the case of silver bromide, his data show that the solubility in thiocarbamide is far greater than in the allyl compound. This gave us hope in our attempts to explain the difference in rapidity of action and ease of control between the thiocarbamide and the allyl thiocarbamide developers.

When we undertook this work we were unable to find any data concerning the relative solubility of silver bromide in the thiocarbamides when unexposed and when exposed to light.[2] We were aware of the fact that even these data would not solve our problem. In dealing with a photographic emulsion, we have found that test tube experiments with a silver halide,

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[1] Valenta: Monatsheft für Chemie, 15, 250 (1894).

[2] NOTE.—After the completion of this paper it was called to our attention that Dr. C. E. K. Mees had worked on the thiocarbamides several years ago (Brit. Jour. Photography, 56, 729 (1909)). He found that the unexposed silver bromide is much more soluble in thiocarbamide than the exposed, since the solubility of silver bromide in thiocarbamide decreases very rapidly in the presence of traces of soluble bromide.

precipitated in the dark, most often give analogous results to the same reaction when applied to the emulsion upon the plate; yet there are decided differences in solubility, porosity, etc., between silver halides precipitated in test tubes, and the silver halide, gelatine, and water complex of the photographic emulsion.

Bancroft[1] calls to our attention the fact that the unexposed silver bromide of a plate is dissolved more rapidly than the exposed portion by such substances as sodium thiosulphate, ammonium hydroxide, potassium cyanide, and ammonium bromide.

We made the broad assumption that such a state of affairs existed in the case of thiocarbamides.

If such a condition exists our data explain most readily a portion of the reasons for the formation of the positives by thiocarbamides. The various colors, and the easy control of such, indicated to us the possible formation of colloidal silver. Unfortunately, we have not been able to study these deposits with sufficient accuracy to give their physical properties.

The combination of "reducer," carbonate, and sulphite, at first serve to develop the latent image. The density of the resultant negative depends upon the concentration of these three constituents together with the degree of exposure. In all of our experiments at a constant exposure the final data which gave the best results, after correcting for any error due to the thiocarbamide, should represent the relative reducing power of the various so-called developers. The carbonate also serves to open the pores of the gelatine, and causes a more rapid reaction. While the reduction of the latent image is taking place, the dilute solution of thiocarbamide tends to dissolve the unexposed emulsion complex more rapidly than the exposed portions. The solvent action takes place with extreme slowness, and as rapidly as the complex

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[1] Bancroft: Jour. Phys. Chem., 15, 313 (1911).

is dissolved it is reduced by some substance to colloidal silver. The deposition of silver upon the unexposed portions of the plate necessarily results, and a positive image is produced.

From a study of our data it would seem as if something other than the carbonate, sulphite, or "reducer" aided in the formation of the positive. It will be remembered that a positive results in the absence of carbonate and also in the absence of sulphite. However, when both are absent a blank plate results. In the absence of a "reducer," a heavily fogged plate always results. The color of this resultant plate is perfectly analogous to the color of the shaded portions of the exposed plate in the corresponding series with the "reducer" present. The problem narrows itself down to the fact that not only must the thiocarbamides act as better solvents for the unexposed than for the exposed emulsion complex, but in the presence of sodium carbonate, sodium sulphite, or sodium hydroxide, in other words, when alkaline, it acts as a "reducing" agent. It seems as if the alkaline thiocarbamides must reduce the dissolved silver complex to silver. The colors of the resultant silver would indicate that it was present in colloidal form.

It was most interesting to observe how readily the results could be checked in test tube experiments. Some unexposed photographic plates were immersed in the dilute solution (2 grams per liter) of thiocarbamide. The resultant solution was poured into four test tubes. To one, was added some of the hydroquinone solution, and nothing happened. To another, some of the sodium sulphite solution was added, and a clouding effect took place throughout the solution. To a third, sodium carbonate was added, and immediately a heavy dark precipitate was thrown down. It required several hours for this precipitate to settle. The addition of sodium hydroxide to a fourth gave the same results as when sodium carbonate was used.

In the case of the test tube experiments a very rapid precipitation occurred. This impressed us with the fact that when the reaction was applied to the photographic plate directly, the gelatine of the emulsion must really play a fairly important rôle. It becomes evident that it must greatly impede the diffusion of the dissolved silver complex, and as a result, permit the reduction to take place almost at the exact point of solution.

Rathke[1] has observed that thiocarbamide can reduce metallic salts from a higher to a lower stage. He found that it acts upon cupric sulphate to form cuprous sulphate momentarily. It would not be amiss to believe that n our particular problem we had the thiocarbamide acting a double rôle.

If our assumptions are not false, it is easy to see why various substituted thiocarbamides should give results of varying control. There must naturally be differences in solubility of the silver complex in these salts. The thiocarbamide which acts slowest as a solvent upon the silver emulsion complex, but which shows the widest distinction between the exposed and unexposed portions, and when alkaline, is the best "reducer," will be the most applicable to the production of direct positives.

It is also perfectly obvious why various brands of plates, as well as different emulsions of the same brand of plate, should give different results. Since all of our work was carried out on the same emulsion of one brand of plates, it makes our data at least comparative. Various emulsions of the same grade will yield plates of different porosities. Each brand of plate will have a different ratio of iodide to bromide, and, of course, this will give an entirely different relative solubility.

Valenta[2] has shown that the following solubility relations exist.

Grams of halide per 100 grams Ag solution of concentration 10 : 100

Salt solution	AgBr	AgI	AgCl
Thiocarbamide	1.87	0.79	0.83
Thiosinamine	0.72	0.09	3.90

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[1] Rathke: Ber. chem. Ges. Berlin, 17, 297 (1884).

[2] Valenta: Monatsheft für Chemie, 15, 250 (1894).

Up to the present time, we can claim that, for the particular plate employed, our results are only comparative. Yet with a systematic study, such results serve admirably to show the real mechanism of the reaction.

Any combination of developers should give a good positive in the presence of a suitable thiocarbamide, provided the solution is sufficiently alkaline, and the concentrations of the constituents are so adjusted that only a very slight negative will be produced during the time that it requires the thiocarbamide to dissolve the unexposed complex, and reduce it to colloidal silver.

The thiocarbamide which will be most efficient, and the easiest of control, must exhibit the greatest difference in solubility towards exposed and unexposed silver emulsions. With compounds where only small differences towards solubility exist, it will be necessary to give far greater exposures, as under such conditions the deposition of silver would tend to be uniform over the whole plate. All of our data indicate that this is the fault with the simple thiocarbamide, as well as with the tetra thiocarbamide ammonium bromide upon our particular brand of plate.

Upon the basis of this theory, that "reducing" agent which tends to develop the high lights more rapidly than the shadows should always tend to give a better positive than the "reducer" which gives a more uniform development. Too high a concentration of "reducer" should always produce positives masked by excessive negative, while insufficient quantities of "reducer" should yield fogged plates. All of our data satisfy these requisites.

A careful consideration of our data points conclusively to the fact that the above explanation for the production of positives by thiocarbamide is, at least, logical. If this theory is correct, it should be applied to other solvents of unexposed silver emulsions.

Since it has been shown[1] that ammonia dissolves the un-

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[1] Bancroft: Jour. Phys. Chem., 15, 313 (1911).

exposed silver complex of an emulsion more rapidly than the exposed portions, it should be possible to produce positives with ammonia and a "reducing" agent. In the light of the best test tube experiments upon the thiocarbamides it seemed possible to save time by determining what substances would precipitate silver from the dilute ammoniacal solutions. An unexposed plate was immersed in dilute ammonia. The resultant solution was separately treated with sodium sulphite, and sodium carbonate, but no apparent action took place. Hydroquinone gave a yellow discoloration, while metol and pyrogallol gave decidedly dark discoloration. The experiments gave results of an entirely different appearance from those with carbonate and thiocarbamide. The precipitates obtained by the thiocarbamide-carbonate reaction were of fair density, while in the case of the metol-ammonia combination the precipitates took place slowly, and presented more of an appearance of a heavy fog. It seemed as if the presence of sulphite increased the rate of precipitation. In spite of the limitations noted in the experiments, it seemed best to make a few experiments.

Kogelmann[1] found that a metol developer containing a good deal of ammonia gave positives. In the absence of complete data we endeavored to determine how far this method was applicable.

A dilute ammonia solution was prepared by diluting 10 cc of concentrated ammonia, sp. gr. 0.90, to a liter.

A great many experiments were made, and very poor results were obtained. The best data which will give positives of poor quality are given in Table IX. These represent the best data available up to the present time. It does not give as good results as are possible, and the study of this is being continued.

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[1] Kogelmann: Eder's "Handbuch der Photographie," 5th Ed., 31, 114 (1902); cf. Bancroft: Jour. Phys. Chem., 13, 547 (1909).

TABLE IX

Exposure in seconds	8
Voltage across tungsten lamp	2.5
Temperature	20–21° C
Time of development	5 minutes
Water	6.9 grams per square inch of surface
Sodium carbonate	0.150 gram per square inch of surface

Concentrations of constituents expressed in grams per square inch of plate surface.

Metol	Sodium sulphite	Sodium carbonate	Results
0.0024	0.476	0.150	A poor blue-black positive.

In this preliminary study positives were obtained in the absence of carbonate of nearly as good quality as those from the best concentration given in Table IX.

The test tube experiments would indicate that in this particular type of developer the metol plays a double rôle. It not only serves as a "reducing" agent in the production of the negative, but it also reduces the dissolved unexposed silver complex as fast as it forms.

A great many positives have been produced by the developer, or a slight modification, as given in Table IX, yet their production is a great uncertainty.

We have not been able to make a thorough systematic study of this system as yet, but it is important to note that the nature of the positive deposit is most analogous to those obtained by the thiocarbamides.

In the absence of available data we have briefly studied the production of positives by means of the amines. In this case, preliminary test tube experiments were made. In the test tube experiments the carbonate and sulphite alone were without any instantaneous effect. Hydroquinone gave a heavy discoloration, and in the presence of sulphite a distinct precipitation took place.

In view of these facts, and with our observations that positives of fair quality could be produced with ammonia we have made a preliminary study of this class of solvents. It has been possible to obtain positives of very fair quality by means of either methyl or ethyl amine and a hydroquinone developer. In these two cases, from the test tube experiments, it would seem as if the active constituents were the amines and hydroquinone. The best data obtained thus far are given in Table X.

TABLE X

Exposure in seconds	8
Voltage across tungsten lamp	2.5
Temperature	20–21° C
Time of development	5 minutes
Water	9.2 grams per square inch of surface
Sodium carbonate	0.118 gram per square inch of surface

Concentration of constituents expressed in grams per square inch of plate surface.

	Amine	Hydroquinone	Sodium sulphite	Results
Methyl	0.0108	0.0048	0.521	Poor, greenish black positives
Ethyl	0.0144	0.0048	0.489	Thin, brown-black positive

The manipulation of the methyl or ethyl amine-hydroquinone developers were as difficult, and gave as uncertain results as the ammonia-metol developer. The color of the deposits were quite different from those of the ammonia-metol combination. Any criticism of one justly belongs to the other. In each case, there is the existing tendency towards the development of a masking negative. The negative seems to act as a screen in preventing the deposition of the positive image. When the content of "reducer" is decreased below a certain limit an effort to eliminate the excessive negative must be exercised with great care to prevent the formation of a heavy fog. With sufficient care, it is possible to produce positives of fair quality with the amines.

In all of the experiments with ammonia and the amines it seemed as if the cause for such poor results is due to the fact that there is but a slight difference in the relative solubilities of the unexposed and of the exposed silver complex. Under such conditions, the manipulative control would be exceedingly difficult.

It is very possible that some type of "reducing" agent other than those heretofore employed will give far superior results.

A. Guebhard[1] found that positives could be obtained by developing underexposed plates, at 8° C, very slowly, in a developer of the following composition: 3 grams of anhydrous sodium sulphite, 1 gram of pyrogallol, 3 grams of sodium carbonate in one liter of water. In this work a development of several hours was required.

It seemed quite probable that he was dealing, possibly to a certain degree, with a phenomenon exceedingly similar to the action as previously outlined. In this case the sulphite undoubtedly plays the rôle of solvent. Although we have not had time to study this type of solvent-developer we have obtained fogged, partial positives after ten minutes development, by using a much larger amount of sodium sulphite than given in the above Guebhard developer. The progress of this work has not been sufficient to warrant further mention.

From our work with the thiocarbamides in particular, and with ammonia and the amines, it seems possible to be able to produce direct photographic positives of excellent character, with ease of manipulation, when the correct solvent is discovered.

Summary

1. A systematic study has been made of the influence of hydroquinone, ortol, pyrogallol, metol, amidol, and eikonogen in the production of direct photographic positives in combina-

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[1] Guebhard: Eder's "Jahrbuch der Photographie," 19, 388 (1905).

tion with thiocarbamide, sodium sulphite, sodium carbonate, and water.

2. The chief rôle of the so-called "reducer" in this type of developer seems to be in a slight reduction of the latent image in order only to create a great difference between the exposed, and unexposed portions of the plate.

3. The "reducer" influences the resultant color of the positive deposit.

4. Many of the positive deposits alter in color during drying.

5. The influence of such substituted thiocarbamides as the allyl, ethyl, and tetra thiocarbamide ammonium bromide has been studied in developers containing each one of the above-mentioned "reducers."

6. The type of thiocarbamide exerts a great influence upon the ease of manipulation and final quality of the positive.

7. The allyl and ethyl compounds are greatly superior to the tetra thiocarbamide ammonium bromide and the simple salt, when used with this particular grade of plate.

8. Allyl thiocarbamide in combination with a hydroquinone or eikonogen developer, or ethyl thiocarbamide in a metol or eikonogen developer, yield exceedingly fine positives.

9. A developer maintained at 20–21° C, of the following relative concentration, was found to give excellent positives: 0.032 gram metol, 0.0037 gram ethyl thiocarbamide, 0.100 gram sodium carbonate, 0.234 gram sodium sulphite, and 9.3 grams of water. A red to a reddish brown positive results.

10. For the average thiocarbamide developer a fairly close relationship between the exposure and concentration of the constituents of the developer must be maintained in order to avoid the excessive production of a negative.

11. In the twenty-four different types of developers considered, the ultimate influence of excessive amounts of each of the constituents was the same. The differences were

merely relative, and of a variation in the color of the deposit. The reds and blues were the predominating colors.

12. Sodium sulphite is not absolutely essential to the production of a positive by means of thiocarbamide, but it improves the quality of the deposit by a restraining action.

13. A blurred positive of a beautiful color is obtained with an allyl thiocarbamide-hydroquinone developer in the absence of sodium carbonate and a much longer time is required for its production.

14. Sodium hydroxide can be used to good advantage in place of the carbonate in the allyl thiocarbamide-hydroquinone developer.

15. To account for the production of positives by thiocarbamide developers, the assumption has been made that the unexposed silver complex of the emulsion is much more soluble than the exposed portion. Thiocarbamides in alkaline solutions tend to reduce that portion of the soluble complex to colloidal silver. The resultant color depends upon the condition and rate of reduction. The concentration of the constituents of the developer must be so adjusted that the solvent action and reduction occur at the same time, and before an excessive negative can be developed. The gelatine favors this action by preventing hasty diffusion, while the carbonate presumably aids in opening up the pores of the gelatine, and dense positives result.

16. All of our data point to the correctness of the above assumption.

17. The most efficient thiocarbamide compound will be that in which the greatest difference in solubility of the unexposed silver emulsion and the exposed portion is in evidence.

18. This principle applies to the production of direct positives by means of an ammonia-metol developer, as well as by a methyl or ethyl amine-hydroquinone developer. Positives of fair quality were obtained with each of these

combinations. These developers presented difficult manipulation.

19. Some substance must exist which readily dissolves the unexposed silver emulsion, and which is without influence upon the exposed emulsion. A "reducer" will be found which will yield a good deposit of silver under these conditions, without a preliminary production of a negative. Ethyl thiocarbamide and metol developer is a step in this direction. When the right combination is found direct positives can be produced without the least manipulative trouble.

Chemical Department,
New Hampshire College

FLAME REACTIONS. I

BY WILDER D. BANCROFT AND HARRY B. WEISER

The Dissociation of Luminescent Gases

In 1861 Kirchhoff and Bunsen[1] wrote that "at the close of this memoir we cannot refrain from touching upon a question, to which, on some future occasion, we must again recur. Among the large number of those salts already examined by us, which, owing to their volatility in the flame, render a spectrum analysis possible, we have not found, in spite of the great variation in the elementary bodies combined with the metal, a single one which failed to produce the characteristic bright lines of the metal. Considering these numerous observations made under the most widely differing circumstances, we might be led to suppose that in *all cases* the bright lines given out by a body occur quite independently of the other elements chemically combined with that body, and that therefore the relation of the elements, as regards the spectra of their vapors, is exactly the same, whether they are free or chemically combined. Yet this supposition is by nc means founded on fact. We have repeatedly insisted that the bright lines in the spectrum of a luminous gas must coincide with the absorption lines which this gas produces in a continuous spectrum of a sufficient degree of luminosity. It is well known that the absorption lines of iodine vapor cannot be produced by hydriodic acid, and that, on the other hand, the absorption lines of nitrous acid are not visible in a mechanical mixture of nitrogen and oxygen. There is nothing to show why an influence of chemical combination upon the absorption lines, similar to that here noticed at low temperatures, should not occur at a white heat. If, however, the state of chemical combination alters the absorption lines of a luminous gas, it *must* likewise alter the bright lines of its spectrum.

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[1] Pogg. Ann., 113, 380; Phil. Mag., [4] 22, 509 (1861).

"From these considerations one would conclude that in the case of the spectra of two different compounds of the same metal, different bright lines may appear; it is however possible that the salts which are volatilized in the flame cannot exist at the temperature of the flame, and are decomposed, so that it may be in reality the vapor of the free metal which produces the lines; and it would then appear quite possible that a chemical compound may produce bright lines differing from those produced by its constituent elements."

Though Kirchhoff and Bunsen had foreseen the possibility of compounds having characteristic spectra, they did not find any actual case of this; but spectra of compounds were obtained, however, by Mitscherlich[1] by introducing into the flame mixtures of ammonium chloride with the chloride of barium, strontium, calcium, copper or bismuth. The spectra of the compounds of copper can very conveniently be obtained pure. At high temperatures there appear the lines of metallic copper. "Hence at a very high temperature of ignition all copper compounds are decomposed into their constituents, whereas these compounds remain undecomposed at a lower temperature—that, for example, of the hydrogen flame. . . .

"From the investigations adduced, it follows, as I have already expressed in an earlier paper, *that every compound of the first order which is not decomposed, and is heated to a temperature adequate for the production of light, exhibits a spectrum peculiar to this compound, and independent of other circumstances.*

"The decomposition of compounds may be caused by the flame gases, or even by the high temperature alone, independent of the gases: thus, for instance, chloride of bismuth, if its solution is used instead of the electrodes in the electrical discharge in chlorine, is decomposed by the high temperature of the electrical discharge alone. Individual compounds re-

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[1] Pogg. Ann., 116, 499 (1862); 121, 459; Phil. Mag., [4] 28, 169 (1864).

sist even this temperature—as, for instance, bromide of copper and iodide of copper, and others, which show the spectrum of the metal together with that of the compound. But if, instead of the solutions which produce a diminution of temperature by their rapid evaporation, the salts themselves are used as solid electrodes, at the then higher temperature most salts are decomposed (as, for instance, these copper salts), and but few compounds remain undecomposed.

"With a great number of metals such a decomposition takes place even under the temperature at which a luminous appearance is observed; hence in this case it has as yet been impossible to observe a direct spectrum of the compounds; and therefore a comparison of the spectra of all compounds has hitherto been impossible. The metals whose compounds are decomposed at such a low temperature, and hence only give the spectrum of the metal itself, are potassium, sodium, lithium, magnesium, zinc, cadmium, silver, and mercury."

"That in the case of sodium compounds the metal actually gives the spectrum, I have shown in the paper already mentioned.[1] In the same paper, by the experiment in which when chloride of potassium is brought into a flame with much chloride of ammonium no spectrum is perceived, I have shown that under certain circumstances metallic compounds of the first order, even when volatile, may give no spectra. This is confirmed by the fact that even the yellow color of the sodium flame almost disappears if a flame containing sodium is brought over strongly volatilizing sal-ammoniac—and further by the fact that if any sodium, lithium, or potassium compound is investigated by method 3 (H and Cl), not even a colored flame, and still less a spectrum is formed. The result is similar if compounds of the alkalies are volatilized in burning sulphuretted hydrogen; it can be distinctly observed that the interior core retains its color perfectly if these compounds are volatilized in it, but that in the outer core, where the sulphur is already burned, a feeble color is formed."

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[1] Pogg. Ann., **116**, 504 (1862).

Plücker and Hittorf[1] obtained multiple spectra with gases. What they have to say about nitrogen is especially interesting. "Not only is the general character of the two kinds of spectra we obtained when nitrogen was heated in our tubes, either by the direct discharge or by the discharge of the interposed Leyden jar, quite different, but the difference is even so great that the bright lines of one of the spectra do not in the least fall within the brighter part of the bands constituting the other. . . .

"For a given nitrogen-tube which without the Leyden jar gives the spectrum of bands, and by means of the commonly used jar the spectrum of bright lines, you may easily select a jar of smaller covering, which, if intercalated, exhibits the curious phenomena of two rival spectra disputing existence with each other. Sometimes one of the spectra, sometimes the other appears; and for moments both are seen simultaneously. Especially the brighter lines of the second spectrum appear in the blue and violet channeled spaces of the first, and, according to the fluctuation of the induced current, either suddenly disappear again or subsist for some time, and constitute with the added fainter lines the second spectrum. . . .

"By these and other experiments it is evidently proved that ignited nitrogen shows two quite distinct spectra. Each bright line of one of these spectra, each of the most subtle lines into which, by means of the telescope, the bands of the other are resolved, finally depends upon the molecular condition of the ignited gas, and the corresponding modification of the vibrating ether within it. Certainly, in the present state of science, we have not the least indication of the connection of the molecular constitution of the gas with the kind of light emitted by it; but we may assert with confidence that, if one spectrum of a given gas be replaced by quite a different one, there must be an analogous change of the constitution of the ether, indicating a new arrangement of the gaseous

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[1] Phil. Trans., 155, 1 (1865).

molecules. Consequently we must admit either a chemical decomposition or an allotropic state of the gas. Conclusions derived from the whole series of our researches led us finally to reject the first alternative and to adopt the other.

"The same spectral tube exhibits, in any succession, as often as you like, each of the two spectra. You may show it in the most striking way by effecting the intercalation of the Leyden jar by means of a copper wire immersed in mercury. As often as the wire is taken out of the mercury we shall have the spectrum of bands; as soon as the communication is restored, the spectrum of bright lines. Hence we conclude that the change of the molecular condition of nitrogen which takes place if the gas be heated beyond a certain temperature by a stronger current, does not permanently alter its chemical and physical properties, but that the gas, if cooled below the same limit of temperature, returns again to its former condition."

The authors are evidently using the words "chemical decomposition" to mean an irreversible change. It is that which they exclude. Their conclusion really is that nitrogen undergoes a reversible change; there is nothing in the experiments to show whether this change is a dissociation, an allotropic change, or some other change.

Wüllner[1] confirms these conclusions. "Nitrogen can only be carried over into the form in which it gives the second spectrum by the sudden passage of relatively large amounts of electricity, such as occurs in the experiments of Plücker when a Leyden jar is placed in the circuit of the induction current or when a Leyden jar is charged by a Holtz machine to the discharging point. In the case of nitrogen one may therefore speak of an allotropic form[2] which yields the second spectrum, which is formed during the sudden discharge of large amounts of electricity, and which changes back into the ordinary form as soon as the temperature of the gas falls."

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[1] Pogg. Ann., 135, 526 (1868).

[2] Plücker and Hittorf: Phil. Trans., 155, 11 (1865).

In a paper published in 1879, Schuster[1] favors the view that changes in the spectrum of a gas indicate molecular changes. "During the first years of spectrum analysis it was generally supposed that a continuous spectrum was characteristic either of a solid or of a liquid body; but as our experimental knowledge gradually increased, it was found that the fact of a body being in the solid, liquid or gaseous state, only indirectly influenced the order of the spectrum. It was believed at first that a chemical compound always showed the spectrum of its individual molecules; in other words, that the vibrations of the molecules were made up of the vibrations of the component atoms. If we accept this theory, then, of course, we have only one explanation of the different orders of spectra, *viz.*, the influence of one molecule on another. According to this view, the state of aggregation of the body must be the direct cause of the change in the spectrum. Since the work of Mitscherlich, however, it had gradually been recognized that a combination of atoms changes entirely the spectrum. This change is not slight but fundamental. The whole vibrating system seems to have been altered; and there is at present, in the majority of cases, no hope that we may consider the vibrations of a molecule to be only the slightly disturbed vibrations of the atoms. We have now a second cause for a change in the different orders of spectra. We need no more look on a continuous spectrum as a line spectrum, disturbed by the shocks of other molecules; but we may explain it by the changes which have taken place in the individual molecule.

"According to this view liquid and solid bodies give generally continuous spectra, not because they are liquid or solid, but because in these states the molecules have a more complicated structure than in the gaseous state. Experiment has to decide between the two theories: the theory of molecular disturbance and the theory of molecular structure.

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[1] Phil. Trans., 170, 37 (1879).

I think that the facts are decidedly in favor of the latter theory."

In a course of lectures before the Royal Institution, W. A. Miller[1] brought out very clearly the prevalent belief that luminescent gases are dissociated at sufficiently high temperatures. "I shall, therefore, in order to give you some idea of the difference between the spectra of the elements and their compounds, ask you to look at a photograph representing the spectra of certain compound substances. I have selected the spectra produced by the compounds of copper, because they resist a higher temperature than most others without undergoing decomposition, and are consequently among those most easily observed. On this photograph you will see a representation of three spectra placed one over the other. The uppermost is the spectrum of metallic copper; the second is the spectrum of cupric chloride, or the compound of copper with chlorine; and the third is that of cupric [cuprous?] iodide, or the compound of copper with iodine. You will observe certain lines in the yellow and the green, which are pretty constant in them all. In the second spectrum, characterized by lines in the blue, we see the effect produced by the combination of chlorine with the copper; and this is again different from the spectrum of the iodide. When Bunsen and Kirchhoff first made their experiments upon the volatilization of bodies in the flames upon which they experimented, they concluded that, whatever the temperature employed, the same spectrum was always produced by the same substance. That statement has since, however, been ascertained not to be absolutely correct. An elementary body may be heated through a very wide range of temperature without experiencing any change in its spectrum, but at a very high temperature new lines not previously observed often make their appearance. . . . Lithium offers an example of this kind. This metal presents a single characteristic line—*viz.*, a brilliant crimson band—which is brought out at

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[1] Chem. News, 15, 276, 285 (1867).

moderate temperatures; but there is another, a fainter line, in the orange, which requires a higher temperature for its development; and, lastly, a very brilliant band in the blue, which requires a still higher heat, such as that of the voltaic arc. . . . Although in the voltaic arc we have a most intense heat, the temperature is not sufficient to cause thallium to vibrate in such a way as to produce more than a single line. The lithium at the same temperature will acquire the power of producing an additional number of vibrations of increased frequency, so that we shall have at least three distinct bands—a band in the red, a band in the orange, and another in the blue.

"Hitherto I have taken the substances in their metallic state, but I wish to show you, in the next place, that if we take certain bodies in their compound condition, we may separate their constituents from each other in the flame of the voltaic arc. For instance, if, instead of taking metallic barium, I take a compound of barium with chlorine, and heat that strongly in the lamp, the chlorine and the barium at that very elevated temperature will be separated from each other; the barium will be converted into vapor, and we shall obtain from the metal its characteristic series of bands, the chlorine spectrum being so faint as to elude our observation under these circumstances. . . . Now I take the carbonate of the same substance, and this carbonate will at the same temperature be resolved into barium on the one hand, which is the glowing gas from which that spectrum was produced, and into other bodies which give out comparatively little light, and which therefore occasion no interference with the results. The spectrum is not quite so bright as the last, for the reason that the carbonate is not a body which is so completely and easily volatilizable as the chloride. The chloride is a substance which, like most chlorides, is readily volatilized by a moderate heat. The carbonate is a body which, at a high temperature, becomes decomposed. It gives off its carbonic acid and produces baryta, and that baryta, in the focus of heat which we have here, is undergoing decomposition. Its oxygen is being separated from it just as when oxide of mercury is moderately heated in a spirit flame, we can separate that into its components—mercury on the one hand, and oxygen on the other. So it is here with baryta: in the intense heat of the voltaic arc, the barium and the oxygen are becoming separated from each other. . . .

"Before I quit this part of our subject, I wish to show you that in particular cases the same gas may give two different spectra. If you send an electric spark through one of these exhausted tubes of nitrogen at a low temperature, you will obtain a spectrum of a particular kind; but the same gas will exhibit at a higher temperature a spectrum which is quite different. . . . These differences are very important when viewed theoretically, though as yet we have no satisfactory explanation of them. It has been supposed that where two spectra occur the bands formed at a low temperature are produced by a substance which is really different from that which gives rise to the bands which are given out by what appears to be the same body at an intense heat. It has been conjectured, though it is by no means proved, that substances which, like nitrogen, give two different spectra, are not elementary bodies, but that at the high temperature they are actually separated into their components, just as we recently separated chlorine from barium and carbonic acid and oxygen from the same metal. But this conclusion is by no means well established, because it is seen that the moment we cease to pass the electric spark, the whole thing is as it was before; and if the substance had been decomposed by the intense heat, it has been as instantly recomposed on the diminution of the temperature."

Cooke[1] is also quite definite in his statements. "At the very high temperatures at which alone gases or vapors become luminous, compound bodies, as a rule, appear to be decomposed, and the elementary atoms dissociated. Hence the

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[1] "Principles of Chemical Philosophy," 197 (1881).

observations with the spectroscope have been almost entirely confined to the spectra of the elementary substances, and our knowledge of the spectra of compound substances is exceedingly limited. In some few cases where the spectrum of a compound has been obtained, it has been noticed that, as the temperature rises, this spectrum is suddenly resolved into the separate spectra of the elements of which the compound consists.

"At a high temperature the metallic atoms of a compound body are far more luminous than those of the other elementary atoms with which they are associated. Hence, when the vapor of a metallic compound is rendered luminous, the light emitted is so exclusively that of the metallic atoms, dissociated by the heat, that when examined with the spectroscope the spectrum of the metal is alone seen; and this is the probable explanation of the fact that the salts of the same metal. . . all show, as a general rule, the same spectrum as the metal itself."

Hasselberg[1] postulates dissociation for the case of the two hydrogen spectra. He says that if his previous reasoning is admitted, "we shall be obliged to assume such a dissociation as the explanation of the displacement of a spectrum by a new one with rise of temperature, and must therefore ascribe the first spectrum [of hydrogen] to a more complicated arrangement of molecules or to a compound of the body with itself. Since, according to the investigations of Wiedemann,[2] in the case of hydrogen a continual rise in temperature produces first a gradual diminution of the spectrum above described, and then upon reaching a certain limit its almost sudden disappearance, these considerations lead us to the view proposed as a second alternative by Ångström, according to which the spectrum belongs to a compound of hydrogen with itself. The heat-equivalent found by Wiedemann for the quantity of energy necessary to transform this spectrum into

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[1] Phil. Mag., [5] 17, 351 (1884).

[2] Wied. Ann., 10, 202 (1880).

that consisting of the three characteristic bright lines, would therefore be nothing else than the thermal equivalent of the corresponding work of dissociation.

"If the views thus explained of the spectroscopic conditions of hydrogen are regarded as justified by facts, we have an easy explanation of the fact that in the spectra of the sun and most stars only the characteristic lines of this gas appear as bright lines or absorption lines, as the case may be, while no trace of the second spectrum is to be detected. The reason is to be found in the enormous temperatures existing in these bodies."

Lockyer[1] of course believes that dissociation occurs in the flame and in the spark.

"I have observed that whether the spectra of iodides, bromides, etc., be observed in the flame or weak spark, *in air*, the spectrum is in the main the same, as maintained by Kirchhoff and Bunsen; but that this is not the spectrum of the metal is established by the facts, *that with a low temperature only the longest lines of the metals are present*, showing that only a small quantity of the simple metal is present as a result of partial dissociation, and that by increasing the temperature, and consequently the amount of dissociation, *the other lines of the metals appear in the order of their length with each rise of temperature.*

"I have convinced myself that this is the spectrum of the oxide, because *in air*, after the first application of heat, the spectra *and metallic lines are in the main the same*, while *in hydrogen* the spectra are different for each compound, *and true metallic lines are represented according to the volatility of the compound, only the very longest lines being visible in the spectrum of the least volatile compound.* . . .

"The heat required to act upon a compound, so as to render its spectrum visible, dissociates the compound according to its volatility; the number of true metallic lines which

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[1] Phil. Trans., 163, 650 (1873).

thus appear is a measure of the dissociation; and as the metal lines *increase in number*, the compound bands *thin out*."

Lockyer apparently assumes, as a matter of course, that the spectrum in hydrogen must be the spectrum of the metal. This conclusion has not always been accepted. Basquin[1] studied the spectra of aluminum, copper, magnesium, silver, sodium, tin, and zinc in hydrogen and says that "with the exception of tin, every metal thus far examined in the rotating metallic arc in hydrogen gives a characteristic set of spectrum lines which are not found in the arc in air. Inasmuch as compounds of hydrogen with some metals are known, I have, in lieu of a better hypothesis, supposed that these lines are due to such compounds formed in the arc." Hartley[2] comments on this to the effect that "sodium hydride cannot exist in a state of vapor; it readily undergoes dissociation, which commences at 200° and is complete at 422°, under barometric pressure; the bands, therefore, are not due to sodium hydride."

The special case of magnesium in hydrogen was studied by Liveing and Dewar.[3] "We have been careful to ascribe this line [at 5210] and its attendant series to a mixture of magnesium and hydrogen rather than to a chemical compound, because this expresses the facts, and we have not yet obtained any independent evidence of any chemical compound of those elements. We have independent evidence that mixtures which are not probably chemical compounds favor the production of certain vibrations which are not so strong or are not seen at all when the elements of those mixtures are taken separately. The remarkable absorptions produced by mixtures of magnesium with potassium and sodium above mentioned belong to this class. We have not been able to obtain the emission spectra corresponding to these absorptions, but in the course of our observations on the arc we have frequently noticed that certain lines of metals present in the

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[1] Proc. Am. Acad., 37, 166 (1901).

[2] Proc. Roy. Soc., 79A, 244 (1907).

[3] Ibid., 27, 495 (1878); 30, 96 (1880).

crucible are only seen or come out with especial brilliance when some other metal is introduced. This is the case with some groups of calcium lines which are not seen, or barely visible, in the arc in a lime crucible, and come out with great brilliance on the introduction of a fragment of iron, but are not developed by other metals such as tin."

In a later paper Liveing and Dewar[1] made a series of observations of the magnesium spark in hydrogen at pressures above that of the atmosphere, using no Leyden jar. "It appears that the compound which had been formed in large quantity by the spark without jar at higher pressures, is only gradually decomposed, and not reformed by the high temperature of the spark with jar. This experiment, which was several times repeated, is conclusive against the supposition that the flutings are merely due to a lower temperature." Hence it was concluded that "the series of lines beginning at wave length 5210 are due to a combination of hydrogen with magnesium, and are not dependent solely upon the temperature."

These phenomena have also been studied by Fowler,[2] who says that "since then the spectrum in question has been generally known as that of 'magnesium hydride,' and as no sufficient reason has appeared for assigning a different origin, this designation has been retained in the present paper.... All the experiments accordingly tend to show that magnesium and hydrogen are together concerned in the production of the flutings, and the simplest supposition is that they originate in the combination magnesium hydride. Assuming such combination of the two elements, it appears to take place directly under the influence of the arc, especially at low pressures, or of some forms of the spark discharge, or by the combustion of the metal in an atmosphere containing hydrogen either free or in combination.

"One of the chief objections to the above explanation

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[1] Proc. Roy. Soc., 32, 198 (1881).

[2] Phil. Trans., 209A, 450 (1909).

of the flutings is that, although the spectrum may be easily produced, the compound itself has not yet been clearly recognized by chemists. Winkler[1] possibly obtained it as part of a mixture resulting from heating magnesium with the oxide in an atmosphere of hydrogen, but no other chemical evidence of the existence of the compound has been brought forward. Further evidence has been sought by an analysis of the deposit formed by the passage of the arc in hydrogen. This consisted in part of thin spherical shells of magnesium, and partly of a fine black or dark gray powder, probably mixed as a rule, with a small proportion of magnesium oxide. The analysis of this deposit was kindly undertaken by Prof. Tilden, who reports that the volume of hydrogen given off on dissolving the sample supplied was always less than the amount calculated on the supposition that it was pure magnesium, and that there was no evidence of a hydride. This was, perhaps, only to be expected from the observation that there was no appreciable absorption of hydrogen during the passage of the arc, but there was the possibility that such absorption might be partly counterbalanced by the liberation of hydrogen from the heated poles.

"In explanation of the spectroscopic observations, on the hypothesis that the flutings are produced by magnesium hydride, it may be supposed that a very small quantity of the compound is competent to produce a brilliant spectrum. The compound would not be unique in this respect, as the cyanogen flutings are ordinarily well developed in experiments on carbon compounds even if only a very small trace of nitrogen be present. Or it may be, as suggested by Mr. Brooks, that the compound is in most experiments decomposed as quickly as it is formed. A perfectly definite conclusion does not at present seem to be possible."

Dufour[2] points out that the gas in a Geissler tube is at

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[1] Ber. chem. Ges. Berlin, 24, 1973 (1891).

[2] Ann. Chim. Phys., [8] 9, 431 (1906).

low pressure and high temperature,[1] conditions which are favorable to dissociation. He considers that the phenomena, shown by Geissler tubes filled with hydrogen, can be accounted for by postulating dissociation along with the theory of ions. His theory "leads to the conclusion that hydrogen is completely dissociated into atoms in the sun and in those stars which do not show the first spectrum of hydrogen."

Mendeléeff[2] believes that free metallic vapors occur in flame spectra; but he seems to attribute the formation of the metals to the reducing action of the flame gases. "A high temperature forms one of those conditions under which compounds most easily decompose; and therefore if sodium or a similar element were a compound, then in all probability it would be decomposed into component parts at the high temperature of the sun. This may already be concluded from the fact that in ordinary spectroscopic experiments the spectra obtained often belong to the metals and not to the compounds taken; this depends on the decomposition of these compounds in the heat of the flame. If common salt be introduced into the flame of a gas-burner, a portion of it is decomposed, first forming, in all probability, with water, hydrochloric acid and sodium hydroxide, and the latter is then partially decomposed by the hydrocarbons, giving metallic sodium, whose incandescent vapor emits light of a definite refrangibility. This conclusion is arrived at from the following experiments: If hydrochloric acid gas be introduced into a flame colored by sodium it is observed that the sodium spectrum disappears, owing to the fact that metallic sodium cannot remain in the flame in the presence of an excess of hydrochloric acid. The same thing takes place on the addition of sal-ammoniac, which in the heat of the flame gives hydrochloric acid. If a porcelain tube containing sodium chloride (or sodium hydroxide or carbonate), and closed at both ends by glass plates, be so powerfully heated that the salt volatilizes, then the

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[1] See, however, Wood: Wied. Ann., 59, 238 (1896).

[2] "The Principles of Chemistry," 1, 563 (1891).

sodium spectrum is not observable; but if the salt be replaced by sodium, then both the bright line and the absorption spectra are obtained, according to whether the light emitted by the incandescent vapor be observed, or only that which passes through the tube. Thus the above spectrum is not given by sodium chloride or other sodium compound, but is proper to the metal sodium itself. It is the same with other analogous metals. The chlorides and other halogen *compounds* of barium, calcium, copper, etc., give independent spectra which differ from those of the metals. If barium chloride be introduced into a flame it gives a mixed spectrum belonging to metallic barium and barium chloride. If besides barium chloride, hydrochloric acid or sal-ammoniac be introduced into the flame, then the spectrum of the metal disappears, and that of the chloride remains, which differs distinctly from the spectrum of barium fluoride, barium bromide, or barium iodide. A certain common resemblance and certain common lines are observed in the spectra of two different compounds of one and the same element obtained in the above-described manner, and also in the spectrum of the metal, but they all have their peculiarities. The independent spectra of the compounds of copper are easily observed. Thus certain compounds which exist and are luminous at a high temperature give their independent spectra. In the majority of cases the spectra of compounds are composed of indistinct luminous lines and complete bright bands, while metallic elements generally give a few clearly-defined spectral lines. There is no reason for thinking that the spectrum of a compound is equal to the sum of the spectra of its elements—that is, *every compound* which is not decomposed by heat *has its own proper spectrum.* This is best proved by absorption spectra, which are essentially only reversed spectra observed at low temperatures. If every salt of sodium, lithium, and potassium gives one and the same spectrum, this must be ascribed to the presence in the flame of the free metals liberated by the decomposition of their salts. Therefore *the phenomena of the spectrum are determined by molecules, and not by atoms*—that is, the molecules of the metal sodium, and not its atom, produce those forms of vibrations which are expressed in the spectrum of a sodium salt. Where there is no free metallic sodium there is no sodium spectrum."

The preceding quotation might be used to prove that Mendeléeff believed in a dissociation by heat alone or that he believed in a reduction by hydrocarbons. Probably he considered both factors as coming in at times. Pringsheim[1] comes out definitely in favor of reduction. "From these experiments it follows that the glowing of sodium in the flame does not take place, as is usually assumed, through the vaporization and dissociation of the salts at high temperatures. If this were the case, the same thing must happen when salts are heated in the furnace and the sodium salts should show the same spectrum in the furnace as in a flame at the same temperature. We must therefore conclude that the luminescence of sodium salts in flames is a consequence of chemical actions which do not take place when the same salts are merely heated in the furnace.

"What are the chemical actions in the flames? Direct oxidation processes are excluded because the salts do not emit light when heated in the furnace in air: it must therefore be reduction processes which give rise to the light.[2] As a matter of fact we are able to cause the salts in the furnace to glow by bringing about these same reduction processes. We can do this either with the same reducing agent which is effective in the Bunsen flame, namely illuminating gas, or with hydrogen, which latter is more convenient owing to the greater chemical simplicity. . . . By these experiments it is proved *that the light emitted by sodium salts in flames is caused by the reduction of these salts, and that this reduction is brought about in the Bunsen flame by the illuminating gas itself.*"

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[1] Wied. Ann., **45**, 443 (1892); **49**, 363 (1893).

[2] See, however, Fredenhagen: Drude's Ann., **20**, 141 (1906).

Smithells[1] finds difficulties in connection with what he calls the currently accepted doctrine. "When a small quantity of common salt or other salt of sodium is introduced into the flame of a Bunsen burner a yellow flame is produced, which is ordinarily ascribed to the vapor of metallic sodium glowing in consequence of the high temperature of its surroundings. The green-blue flame due to copper chloride under the same circumstances is attributed to the incandescent vapor of copper chloride. With calcium chloride the red flame which is obtained is said to be due to the vapor of calcium chloride and of calcium oxide. These may be taken as typical cases.

"The authority for these views dates back, as is well known, from the earliest days of spectrum analysis. One or two questions connected with them which are at once obvious to the chemist are as a rule passed over in silence. If it be asked, for instance, how does sodium vapor become free in the flame, what answer is to be given? The usual answer, I believe, has been that the salt is dissociated, notwithstanding that we have no other evidence of the dissociability of sodium chloride at any attainable temperature.[2] Another explanation that I have seen, and that only once, is given by Mendeléeff in his 'Principles of Chemistry' (1, 563). He says that the NaCl is acted upon by steam in the flame to produce NaHO and that this is subsequently reduced by the carbonaceous matter of the flame. Again, it may be asked, how is it that copper chloride, which is known to lose its chlorine at quite moderate temperatures, can not only be vaporized but be made incandescent in a flame, and in a flame too which contains reducing gases.

"The solution of the difficulties here presented is not so obvious that it should be withheld, yet I have been unable, in searching the literature of spectrum analysis, to find any discussion of these fundamental questions.

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[1] Phil. Mag., [5] 37, 245 (1894).

[2] Sir G. G. Stokes informs me that he has never entertained this view, but it has certainly been widely expressed.

"I propose now to discuss some cases of flame-coloration in respect to the chemical reactions by which they are accompanied in the flame.

"The characteristic yellow flame of sodium with the D-line spectrum represents, as is well known, the most easily obtainable flame-spectrum. It is yielded by all salts of the metal in the flame of coal-gas or hydrogen. It is quenched, according to Mitscherlich,[1] if hydrochloric acid be supplied in excess along with the sodium salt, which may be done by adding an excess of ammonium chloride to the bead. The yellow tint is also, according to Mitscherlich, not yielded in the flame of hydrogen burning in chlorine when these gases are burnt in an oxy-hydrogen burner. I have repeated Mitscherlich's experiments with great care, using the flame of hydrogen in chlorine and of chlorine in hydrogen. So long as any oxygen remains in the gases the flame shows a distinct yellow color when a bead of a sodium salt is introduced into it. As the oxygen is removed by a current of purified gas (chlorine or hydrogen) the yellow color fades until it is imperceptible to the eye. Viewed with the spectroscope the D-line shows a corresponding diminution of intensity, and in entire absence of oxygen, is doubtless extinguished. As I have only once succeeded in entirely obliterating it, I do not wish to speak positively. The fact that the red line of lithium is easily quenched under similar conditions confirms the belief that the same would be the case with the more sensitive sodium, if all traces of oxygen could be removed.

"It appears to me that the above facts present great chemical anomalies and difficulties. If we are to make the common assumption that the yellow flame is due to sodium vapor, the element must be liberated either by dissociation, by heat or reduction. Of dissociation by heat we have no independent evidence, and it is gratuitous to suppose that it should take place in a coal-gas flame and not in the flame of

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[1] Pogg. Ann., 116, 499 (1862); 121, 459 (1864).

hydrogen burning in chlorine. If the process is one of reduction we have to go beyond our experimental knowledge to suggest an explanation. Thus the liberation of sodium from common salt in a hydrogen-flame must be due either to the union of hydrogen with chlorine to form hydrochloric acid and free sodium, or to the action of steam which forms hydrochloric acid and sodium hydrate or oxide, the latter being then reduced to the metal by the hydrogen. If it is said that hydrogen may decompose salt in the first way at high temperature, it must also be remarked that hydrochloric acid itself decomposes at high temperatures. If, on the other hand, the steam itself is the active agent, it is certainly taking a liberty to invoke its presence to act on the salt, and to ignore its probable interference with any reduction of the oxide or hydrate to be subsequently effected by hydrogen.

"If we can explain the coloration of a hydrogen flame by salt, it will of course be easy to explain it in the case of a coal-gas flame. The suppression of the color in a hydrogen-chlorine flame can only be explained from the point of view of reduction by assuming that the conjoint action of oxygen and hydrogen is necessary for the decomposition of the sodium chloride, the hydrogen taking the chlorine and the oxygen the sodium, the sodium oxide being thereupon reduced by hydrogen.

"The only alternative to the above explanation is, so far as I am aware, that indicated by Arrhenius[1] in his experiments on the electrolytic condition of the heated vapors of salts. Arrhenius supposes that when salt is supplied to a flame, sodium hydrate is formed by the influence of steam and that the hydrate then undergoes partial ionic dissociation, the liberation of sodium taking place without the intervention of chemical action.[2] The process is thus regarded as analogous to the dissociation of electrolytes in dilute

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[1] Wied. Ann., 42, 18 (1891).

[2] [There seems to be a tacit assumption that sodium is the same as sodium as ion.]

aqueous solution. I cannot attempt to summarize the experimental evidence by which Arrhenius seeks to establish his interesting theory: If true, it would certainly remove many difficulties which have been met with in attempting to account for the phenomena of flame coloration on purely chemical grounds.[1]

"With regard to Arrhenius's view of the matter, I will only remark at present that the liberated sodium must sooner or later meet with oxygen, and burn. If the yellow light of the flame is due to the vibrations of ionic sodium, it would seem likely that the light emitted during combustion of the sodium, and due presumably to sodium oxide, should be different. Now the light from sodium burning in oxygen gives a continuous spectrum and it is possible that the faint continuous spectrum which accompanies the line spectrum of sodium salts heated in a flame may be due to the combustion of the sodium, while the line spectrum is due to the mere vibration of the sodium ions.

"I may summarize the views above expressed as follows:

"1. There is no evidence for, but much against, the supposition that sodium salts when introduced into a flame are dissociated by heat so as to liberate the metal.

"2. There is great difficulty in accounting for the reduction of the metal by purely chemical processes.

"3. Arrhenius's hypothesis of ionic dissociation in flames is a chemically acceptable way of accounting for the liberation of sodium when its salts are heated in flames.

"4. There is no direct and no decisive evidence that the sodium spectrum is the direct consequence of the chemical action in which the atoms are engaged."

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[1] In addition to those already pointed out I may adduce the following: when a flame colored by a bead of sodium is viewed against a bright background of D-light, it is seen to be surrounded by a black mantle. If this is due to absorption by free sodium, then the element must be able to exist in an atmosphere of steam and carbon dioxide. This is utterly opposed to our ordinary notions of the chemical relations of the substances in question, but would present no difficulty from the point of view of Arrhenius.

A slightly different point of view is taken by de Watteville[1] as a result of experiments on flame spectra, using a Gouy sprayer. "An inspection of the preceding tables will have shown that the lines in the spectra produced under the conditions of my experiments are much more numerous than is the case when the salt spray is not previously mixed with the gases which react to form the flame, but is introduced in some other manner. In the latter case it does not really enter into that zone of flame where the most intense chemical reactions are occurring and where the temperature is most elevated. Two different causes might be suggested in order to explain this increase in the number of the lines.

"The flame is divided into two quite distinct portions: an inner one which is reducing in its action, and another one which is oxidizing on account of the presence of air in excess. In the working of the sprayer the metallic salt is forced to pass in succession through these two regions, *i. e.*, from the reducing region to the oxidizing region. It is possible that, during the passage across the boundary separating these two regions, there is a period, possibly very short, in which the metal, liberated from its combination, exists in the state of metallic vapor. The atom is at this moment in the hottest portion of the flame, namely, that which surrounds the blue inner cone and which is surrounded itself by the external portion of the flame. Here it may undergo a breaking-up or in any case a modification of its physical or chemical constitution. In support of this view, one might mention the great changes produced in all the properties of iron, even in the solid state, by variations of temperature of much smaller range than those which occur in the flame. The metallic vapor, thus modified, passes in succession through zones of the flames of gradually decreasing temperature, and in which it exists in other intermediate states which might be called 'states of less advanced dissociation.' . . .

"It seems to me that a satisfactory explanation of the

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[1] Phil. Trans., 204A, 160 (1904).

phenomena I have observed may be obtained by considering them as the results simply of variations of temperature. Of course, it cannot be denied that spectra may be formed by other means than a pure and simple elevation of temperature, but these methods ultimately reduce themselves to chemical transformations and thermal changes. This temperature hypothesis, which accounts in the simplest way for the production of the spectra, finds considerable support in the fact that the stars give spectra which are similar in their constitution to those obtained in the laboratory by electrical methods. It is difficult to imagine any other but a purely thermal cause for the luminosity of stars."

Hartley[1] comes out strongly in favor of the view that the free metals are produced in the flames by reduction.

"It has already been shown that aluminum can be reduced from its oxide in the oxyhydrogen flame, that it colors the flame and emits the two lines λ3967 and λ3946. It was concluded that bands which have been attributed to the oxide are in reality metal bands.[2] Bands of beryllium and lanthanum were also reduced from their oxides; the greater volatility of metallic beryllium[3] caused the band spectrum to be photographed without the lines.

"I have now arrived at the conviction, from additional evidence presently to be adduced, that calcium and strontium are also produced in the oxyhydrogen flame by thermal-chemical reduction of their oxides and sulfides.

"The question of the reduction of the oxides of the dyad and triad groups is quite different from that of the oxides of the alkali metals, because compounds of the latter are not only easily volatilized, but it has been proved by St. Claire Deville that, in the manufacture of the alkali metals, the oxides are thermochemically dissociated, and then reduced by carbon entering into immediate combination with the dissociated oxygen."

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[1] Proc. Roy. Soc., 79A, 242 (1907).

[2] Trans. Roy. Dublin Soc. [2,] 7, 346 (1901).

[3] This was observed by Pollok in its reduction by the arc.

Spectro-chemical Evidence from Anhydrous Flames and Dehydrated Salts.—"By an anhydrous flame is meant one in which water is not a product of combustion. Any salt which yields the spectrum, or imparts the characteristic color of the metal to such a flame, is excluded from the view of Arrhenius that vaporized salts are first hydrolyzed by water-vapor in the flame, that the hydroxides thus formed undergo ionization, and the spectra are caused by the metallic cations. Smithells, Dawson, and Wilson first applied this test to alkali salts, by heating them in the flame of burning cyanogen.[1] Lenard also has observed that sodium salts color the flame of carbon disulphide. The authors aforesaid suggest that a chemical reduction takes place and the metal then colors the flame. I have extended this inquiry by placing anhydrous salts in the flame of carbon monoxide.... On introducing into the flame recently ignited carbonates of lithium, sodium, and potassium, even without heating the platinum tube, beautiful spectra were observed, such as are visible in the flame of a Bunsen burner. It was very difficult to see the red line of potassium about λ7660, but the green glow and a group of green lines about λ5800 were observed. Experiments were tried in both the inner and outer cones, but only when the substance was heated at the tip of the inner cone could the group of green lines be seen. In this instance it is not reasonable to suppose that sufficient water could gain access to the flame to give rise to hydrolysis, and, in fact, hydrolysis could not take place.

"The same experiments were repeated with the oxides, carbonates, and nitrates of calcium, strontium, and barium; but although the platinum tube was heated to bright redness, there was no trace of a spectrum of either bands or lines in any case. Calcium, strontium, and barium chlorides, on the other hand, showed superb spectra of the chlorides, apparently identical with those produced by heating the same salts in a coal-gas flame saturated with hydrochloric acid. The tem-

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[1] Proc. Roy. Soc., 64, 142 (1899).

perature of this carbon monoxide flame, which was from 50 to 75 mm long, is higher than that of a Bunsen burner of the same size,[1] and can raise a larger mass of material to a higher temperature.[2] Here we have evidence that the metals of the alkalies behave quite differently from those of the alkaline earths; calcium, strontium, and barium chlorides are volatile without decomposition, for they fuse and remain clear liquids without showing turbidity for as long as is necessary to observe their spectra. Inasmuch as they appear to yield their own spectra, they behave like calcium fluoride when placed in the oxyhydrogen blow-pipe flame, and doubtless other similar fluorides and phosphates. The most important facts ascertained so far are, first, the alkaline earth oxides are not volatile in the carbon monoxide flame, or, if they are, they show no spectrum; second, the flame is a powerful reducing one to all oxides with a heat of formation not greater than that of zinc oxide, but the oxides in question are not reduced; thirdly, the temperature of the flame is higher than that of a Bunsen burner, and over a large area it is nearly as high as that of the oxyhydrogen flame; fourthly, the chlorides are volatile in an anhydrous flame, but the stability of the chlorides in such a flame is somewhat doubtful, as they may undergo dissociation.

"The action of the cyanogen flame is very different from that of the flame of carbon monoxide, because cyanogen is a very powerful reducing agent.

"When calcium oxide was introduced on a platinum wire into the flame of cyanogen burning in air, there was no action low down in the flame, but when the substance was placed at the tip of the inner cone, there was a magnificent display of the same spectrum as that seen when calcium metal is burnt in air, and with no trace of the cyanogen bands. The effect on baryta was tested in a similar manner, by making pure

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[1] Jour. Chem. Soc., 63, 844 (1896).

[2] Platinum wire 1/40th mm in thickness can be melted into a globule in any part of the flame.

barium carbonate into a stiff paste with water, and moulding it round a loop of platinum wire. On placing this in the flame at the same point, an equally fine spectrum of barium was obtained. In both instances the spectra were identical with those photographed when the same compounds were placed in a Mecke burner, but the brilliancy and intensity of the rays were greatly increased. Beyond all doubt these spectra are the spectra of the metals.

"The deductions from these facts are, that the lines and bands seen in the oxyhydrogen flame are certainly not the spectra of the oxides, because if the difference between this and the carbon monoxide flame were simply one of temperature, the emission spectra of oxides and sulphides should be quite as easily produced in a carbon monoxide flame as in one of hydrogen. Finally, carbon monoxide was burned with oxygen in a Deville blow-pipe and still no spectrum of calcium or strontium was seen, except when traces of chloride were present. The salts were supported on very thin slips of Donegal kyanite.

"The presence of hydrogen in the flame is, therefore, a necessary element in some chemical reaction which leads to the reduction of the sulphides or oxides to the metallic state. The temperature of these flames, which can melt platinum, is sufficient to effect the thermo-chemical dissociation of water-vapor, and it is probable that in this lies the cause of the spectra appearing."

While discussing the question whether the metals can be obtained by the reducing action of the flame gases, Hartley[1] points out a number of interesting facts.

"The flames from coal-gas, hydrogen, and carbon monoxide, respectively, when burning in air, have a temperature as high as that of the melting point of platinum, 1775° C. This temperature exceeds that of the metallurgical furnaces, in which sodium, potassium, cadmium, zinc, and magnesium are reduced and distilled on an industrial scale....

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[1] Proc. Roy. Soc., 79A, 255–261 (1907).

"An important fact may be observed here, namely, that whereas the banded spectrum of potassium is comparatively easy to obtain, that of lithium is very difficult, more difficult than that of sodium, and even the continuous rays are very weak. The same must be said of rubidium, with the additional remark that its band spectrum has never yet been seen.[1] This, undoubtedly, in part arises from the high value for the heat of formation of the oxides of these metals, and it is obvious that these particular properties of lithium serve to explain why the continuous glow observed by Lenard in the case of lithium is weaker than that of either sodium or potassium, which led him to remark that it was probably a property peculiar to that element. Even rubidium carbonate was reduced by mixing with carbon and heating to a particularly high temperature (Bunsen), but the greater volatility of rubidium compounds may facilitate their dissociation.

"It is quite evident, then, that with the fusible and volatile oxides of sodium, potassium, and rubidium, reduction can be effected at a temperature not exceeding a white heat and probably about 1400° C, certainly below the temperature of melting platinum, and below the highest temperatures of the coal-gas, the hydrogen, and the carbonic oxide flames.

"Hence I conclude that the banded spectra of lithium, sodium, and potassium observed at the temperature of the oxyhydrogen flame are the spectra of the metals....

"The haloid salts of the metals of the alkaline earths are volatile without decomposition in flames supplied with the halogen hydrides. They are also volatile without decomposition in a dry carbonic oxide flame. Here, then, we may probably have the spectra of salts and not of metals. In a hydrogen or coal-gas flame the salts are hydrolyzed and converted into oxides by heat; this is a fact well known....

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[1] A note appears on one of my photographs that there are just faint indications of bands in the strong continuous spectrum.

The effect of water vapor in the flame is an endothermic reaction when the chloride is a solid.... When the chlorides are vaporised in the flame, these endothermic values must be much less and the reactions are easily reversed, as we know by experience when gaseous hydrochloric acid or much ammonium chloride is passed into the flame. We can see clearly also why it is that the carbonic oxide flame does not decompose these salts, the heat of combination of the chlorides being much in excess of that of the oxides, and the reducing power of carbonic oxide, which is the converse of the energy of formation of carbonic oxide, much less....

"We have now to take into consideration the reducing power of hydrogen at high temperatures in flame reactions. There are two values for the production of gaseous water, 58.1 Cal and 50.6 Cal, the smaller of which is at a temperature approaching 2000°, which we may consider to be the highest temperature of all flames capable of melting platinum. The decreasing value at high temperatures is evidence of the dissociation of water-vapor, which we know does occur at the temperature of white hot platinum. Now both the above values are below that obtained by the combustion of carbon monoxide, 68.2 Cal; it is therefore unnecessary to consider a coal-gas flame apart from one fed with hydrogen, for many of the reduction and dissociation phenomena that can take place in the latter may occur in the former.

"The high temperature tends to the dissociation of other oxides than water, and the alkaline earths are most certainly volatilized in Deville's blow-pipe flame, whether they are first dissociated or not. Furthermore, reduction processes are carried on in the solid material, which have hitherto not been suspected, such as the reduction of strontium and barium sulphate to sulphides and of beryllia and alumina to the state of metal....

"The actual energy supplied before alumina is reduced by carbon, carbon monoxide, or hydrogen is —82.5 Cal, —62.7 Cal, or —72.9 Cal, respectively. The carbon monoxide value is thus shown to be less than that in either of the other two reactions. It has already been proved,[1] first, that alumina is reduced to the metallic state in the oxyhydrogen flame; secondly, that the reduction takes place more easily when the alumina is mixed with some dense form of carbon. In the first instance, the flame alone supplied hydrogen only as the reducing agent, consequently, the energy required for every atom of oxygen removed was 72.9 Cal in the form of extraneous heat which was necessary not only for initiating the process, but also maintaining it. When solid carbon was used this was a somewhat higher figure, being 82.5 Cal, but this very reduction process with solid carbon would result in the formation of carbon monoxide which could then operate upon another molecule of alumina, which places the extreme limits of the energy required for reduction as between 63 Cal and 82.5 Cal. From this it would appear that *any reducing process may be carried out in the oxyhydrogen flame by a purely chemical action if the extraneous energy required to initiate and maintain the action does not exceed*[2] *84.8 Cal per atom of oxygen removed*....

"Beryllium is certainly reduced from the oxide by the oxyhydrogen flame, and, as far as we know, beryllia is not a volatile oxide, nor is it fusible. The reduction must, therefore, be the result of a purely chemical action, and it must also be of a highly endothermic character, as may be seen from the equation following:

$$BeO + H_2 = Be + H_2O - 97.4 \text{ Cal.}$$

"It may be inferred from the evidence afforded by the flame spectra, that at these high temperatures the infusible and non-volatile metallic oxides are in a peculiarly active condition, having absorbed a large amount of energy from the flame, so that they are approaching the condition of dissociation and are, therefore, subject to chemical interactions with

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[1] Hartley and Ramage: Jour. Chem. Soc., 79, 63 (1901).

[2] This is the figure for the heat of formation of zinc oxide, 84.8; the value calculated for the reduction of alumina is 82.5 Cal.

the reducing gases, which otherwise would have no power to reduce them. But in the cases referred to, the reducing gas is hydrogen, and in all probability it is not the hydrogen supplied to the flame in the molecular condition, but hydrogen in the atomic or nascent state, resulting perhaps from the dissociation of water, the product of combustion in another part of the flame, which carries with it the additional charge of energy which enables it to initiate and complete the reduction process."

The conclusions drawn by Hartley were:

1. The oxides of calcium, strontium and barium are not dissociated by heat alone, because they show no spectrum in a carbon monoxide flame.

2. They are reduced by the combined action of heat and hydrogen in the oxyhydrogen flame and by the action of cyanogen in the cyanogen flame.

3. The flame coloration is due to the metal, because not only is the flame spectrum from lime essentially the same as that of the metal calcium, but also the heats of formation of CaO, SrO, and BaO have very nearly the same value, and that where calcium oxide can be reduced the other oxides could, on that account, undergo a similar reduction. Whether the compound of strontium or barium in the flame be a sulphide or an oxide, the same spectrum is emitted, but there is some uncertainty as to whether the barium sulphide is not converted into oxide by water-vapor in the flame. The explanation given by Lenard, of the flame coloration of the alkali salts, appears to be inapplicable to the coloration of the carbon monoxide flame by the haloid salts of the alkaline earth metals.

Thermochemical data have a distinct fascination for many people; but it is dangerous to play with them when dealing with reversible dissociations. The reason that we do not get the spectrum of certain metals in the hydrogen-chlorine flame is because the dissociation is forced back by the hydrochloric acid and not because of any conclusion that one can draw from thermochemical data. Fredenhagen[1] makes a similar mistake in a different way and draws the conclusion that people have been studying the spectra of the oxides without knowing it.

"From the preceding compilation we see that all the elements which have been studied give fundamentally different spectra in the Bunsen flame and in the hydrogen-chlorine flame. How is this to be reconciled with the view of Kirchhoff and Bunsen that the free metallic vapors are the radiation centres for the flame-spectra? Since the hydrogen-chlorine flame has about the same temperature as that of the ordinary Bunsen flame, there are no marked differences of temperature between the flames such as might give rise to different spectra. One might consider the possibility of the concentration of the free metallic vapors being very much less in the hydrogen-chlorine flame than in the Bunsen flame. So marked a difference in the dissociation in the two flames is, however, very improbable. In fact, one would expect the reverse state of things with the alkali metals because the chemical properties of the alkali chlorides would make us expect them to be dissociated considerably more at a given temperature than the corresponding oxides of the alkali metals. Also, comparative measurements of the conductances of hydrogen-chlorine and Bunsen flames containing vapors of alkali salts show that the dissociations are much the same in the two flames.

"It is apparently not possible, therefore, to reconcile the view of Kirchhoff and Bunsen as to the radiation centres for the flame spectra with the preceding experiments. Since these experiments show that each element has different spectra in the flames in which it forms different compounds, and has the same spectrum in the flames in which it forms the same compound—for instance, the oxides in all oxygen flames—it seems to me that the only possible explanation is that all

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[1] Drude's Ann., 20, 149 (1906).

the flame spectra which have been considered are spectra of compounds.

"This point of view does away with a difficulty peculiar to the previous conception, namely, that only metals give flame spectra, and not metalloids. This new point of view also brings about rather radical changes in our conclusions as to the spectral evidence for the presence of elements in the stars. From the coincidence of lines in the solar spectrum with the D-lines, we not only conclude, as before, that sodium occurs in the sun; but we must also postulate the simultaneous occurrence of sodium and oxygen."

In a recent article Schuster[1] lays stress on the part played by ions.

"Compounds generally show spectra of resolvable bands, and if an elementary body shows a spectrum of the same type we are probably justified in assuming it to be due to a complex molecule. But that it may be given by the ordinary diatomic molecule is exemplified by oxygen, which gives in thick layers by absorption one of the typical sets of bands which were used by Deslandres and others to investigate the laws of distribution of frequencies. These bands appear in the solar spectrum as we observe it, but are due to absorption by the oxygen contained in the atmosphere.

"If oxygen is rendered luminous by the electric discharge, a series of spectra may be made to appear. Under different conditions we obtain (*a*) a continuous spectrum most intense in the yellow and green, (*b*) the spectrum dividing itself into two families of series, (*c*) a spectrum of lines which appears when a strong spark passes through oxygen at atmospheric pressure, (*d*) a spectrum of bands seen in the cathode glow. We have therefore five distinct spectra of oxygen apart from the absorption spectrum of ozone. To explain this great variability of spectroscopic effects we may either adopt the view that molecular aggregates of semi-stable nature may be found in vacuum tubes, or that a molecule may gain or

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[1] "Encyclopaedia Britannica," 11th edition, 25, 630 (1911).

lose one or more additional electrons and thus form new vibrating systems. It seemed that an important guide to clear our notions in this direction could be obtained through the discovery of J. Stark, who examined the spectra of the so-called canal rays. These rays are apparently the trajectories of positively charged particles having masses of the order of magnitude of the gaseous molecules. Stark discovered that in the case of the series spectrum of hydrogen and of other similar spectra the lines were displaced, indicating high velocities; in other cases no displacement could be observed. The conclusion seemed natural that the spectra which showed the Doppler effect were due to vibratory systems which had an excess of positive charge. More detailed examinations of the canal rays of J. J. Thomson and others have shown, however, that they contain both neutral and charged molecules in a relative proportion which adjusts itself continuously, so that even neutral molecules may partake of the translatory motion which they gained while carrying a charge. No such conclusion can therefore be drawn, as Stark[1] has more recently pointed out, respecting the charge of the molecule which emits the observed spectrum. Nevertheless, the subject is well worth further investigation.

"Previous to Stark's experiments, P. Lenard[2] had concluded that the carriers of certain of the lines of the flame spectra are positively charged. He draws a distinction between the lines of the trunk series to which he assigns neutral carriers, and the lines of the two branch series, the carriers of which are electrically charged. The numerical relations existing between the trunk series and the branch series make it somewhat difficult to believe that they belong to different vibrating series. But while we should undoubtedly hesitate on this ground to adopt Fredenhagen's[3] view that the two branch series belong to the element itself and the trunk

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[1] Phys. Zeit., 11, 171 (1910).

[2] Drude's Ann., 17, 197 (1905).

[3] Phys. Zeit., 8, 735 (1904).

series to a process of oxidation, we cannot press the argument against the view of Lenard, because the addition or subtraction of an electron introduces two vibrating systems which are still connected with each other and some numerical relationship is probable. Whatever ideas we may form on this point, the observations of Stark and Siegl[1] have shown that there is a Doppler effect, and therefore a positive charge for one of the lines of the trunk series of potassium, and E. Dorn[2] has found the Doppler effect with a number of lines of helium, which contain representatives of the trunk series as well as of the two branch series. These facts do not countenance the view that there is an essential electric difference between the vibrating system of the three members of a family of series.

"It is probable, however, that the above observations may help to clear up some difficulties in the phenomena presented by flames. While we have seen that the radiation of sodium vapor has an intensity corresponding to that of the pure thermal radiation at the temperature of the flame, other flames not containing oxygen (*e. g.*, the flame of chlorine in hydrogen) do not apparently emit the usual sodium radiation when a sodium salt is placed in them. In the light of our present knowledge we should look for the different behavior in the peculiarity of the oxygen flame to ionize the metallic vapor."

Although this review of the subject shows that the consensus of opinion is strongly in favor of the view that the elements are set free when salts are introduced into flames, very little seems to have been done in the way of testing this belief in any other way than spectroscopically. Salet[3] precipitated sulphur from a hydrogen-air flame. "If the blue color of the flame containing a sulphur compound is really due to the presence of free sulphur in a portion of the flame where the

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[1] Drude's Ann., 21, 457 (1906).

[2] Phys. Zeit., 8, 589 (1907).

[3] Ann. Chim. Phys., [4] 28, 45 (1873).

temperature is moderately high, it would be interesting to isolate the sulphur and to estimate the temperature at least approximately. The isolation of the sulphur can be accomplished by introducing into the flame a substance which is cold enough to condense the sulphur and hot enough to prevent the condensation of the water formed by the combustion. These conditions can be realized by using as a cold body a tube of platinum through which passes a very slow current of water. The water soon boils in the tube and the temperature of the latter is thus kept at 100°. If traces of sulphurous acid are introduced into the flame, a sheaf of blue light surrounds the tube for a certain distance and, in time, this portion of the tube becomes coated with a film of sulphur. If the water is allowed to flow through the platinum tube more rapidly, the water vapor, formed in the flame, condenses and trickles down the tube. This condensed water contains sulphur, which gives it a milky appearance, and sulphuric acid which makes it distinctly acid. The sulphuric acid is formed even when the sulphur is introduced into the flame as hydrogen sulphide. This should not surprise us because the ordinary product of the combustion of sulphur, sulphurous acid, decomposes at a high temperature into sulphur and sulphur trioxide (H. Deville). Also, the outer zone of the flame has a very strong oxidizing action, as is well known. Water and nitrogen, for instance, oxidize in the outer zone to hydrogen and nitric acid.

"To determine the temperature of the blue portion of the chilled sulphurous flame, a very thin piece of platinum wire was introduced into the flame. Far from melting, the wire scarcely becomes luminous even in otherwise complete darkness. The colored sulphur vapor is therefore luminous at a very low temperature, one at which sodium gives almost no light; for if one cools a hydrogen flame colored yellow by sodium, the cold body seems to be surrounded by a black layer which is thicker than the luminous layer due to sulphur. This experiment proves directly that the temperature of the flame scarcely exceeds red heat and, further, that above this temperature the sulphur lost its remarkable power of emitting light. If one allows the metal, which has served as a cold body, to heat up gradually, one notices that the blue layer becomes paler and paler, disappearing completely when the metal gets above red heat. It is certain that free sulphur is still present in the flame for one cannot assume that hydrogen sulphide could resist this high temperature without losing its sulphur and yet one cannot detect the presence of hydrogen sulphide in the flame. At this temperature sulphur vapor has attained its normal condensation and the physical properties of this sulphur differ undoubtedly from those of the heavy and absorbing vapors which we know."

Hodgkinson[1] states that "a moderate sized sulphur flame will deposit sulphur on a cold object in it." He is speaking of the flame of sulphur burning in air and he cites this experiment to prove that sulphur volatilizes before it burns. Hodgkinson considers that the sulphur deposited on the cold object is sulphur which has been volatilized and which has not yet been burned. He does not consider the possibility of free sulphur coming from sulphur dioxide.

Smithells[2] has shown that carbon is set free in a hydrocarbon flame. "As it has been repeatedly shown that the dark, central part of a luminous flame is a region of no combustion, there only remains now one question for solution—how is the carbon separated in the yellow, luminous region? It would seem scarcely necessary after a perusal of Kersten's paper[3] to argue this point at any length. The doctrine that the hydrogen of a hydrocarbon burns before the carbon when the supply of oxygen is limited is not borne out by any experiments of which I am aware, with the possible exception of those of Berthelot and Vieille.[4] From the fact that the velocity

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[1] Chem. News, 61, 96 (1890).

[2] Jour. Chem. Soc., 61, 223 (1892).

[3] Jour. prakt. Chem., 84, 290 (1861).

[4] Comptes rendus, 98, 705 (1884).

of explosion of hydrocarbons rich in hydrogen approximates to that of hydrogen itself, they conclude that the hydrogen burns before the carbon. The experiments of Dalton, Kersten, E. von Meyer, and those recorded in the preceding paper, all point to exactly the opposite conclusion, namely, that the carbon burns preferentially to the hydrogen. If this conclusion is accepted, we can explain only the separation of carbon in a luminous flame as due to a *decomposition by heat*, whereby a given hydrocarbon is split up into carbon and hydrogen, or carbon and some more richly hydrogenized hydrocarbons. Hydrocarbons are well known to undergo such decompositions when passed through hot tubes.

"A very simple experiment, which seems sufficient to prove the truth of this view, is made by introducing a circular loop of thin wire into any small gas flame in which the luminous part is only slightly developed. The immediate result is that the luminous part disappears and the flame presents the simple structure of a non-luminous flame, at the same time becoming slightly larger. Now if the flame is luminous, because the hydrocarbons in the middle being short of oxygen, the hydrogen burns first, the intrusion of the wire will block out and still further limit the supply of oxygen, and so either increase the area of luminosity or cause the escape of unburned carbon. If, on the other hand, the luminosity is due to the heat of the external perfectly burned layers decomposing the hydrocarbons, then the intrusion of the wire by tapping the heat should diminish the luminosity, and the hydrocarbons which previously gave light should pass on until they obtain enough oxygen to burn as those hydrocarbons on the exterior of the flame. The flame, therefore, would become larger and non-luminous. This is exactly what happens in the experiment.

"The above experiment only holds good if the wire conducts heat away at a certain rate. If the flame be relatively large, the introduction of the wire may produce an opposite effect, for, while checking the separation of carbon (to an appreciable extent), it will also cool down the carbon which is separated and so cause some of it to escape as smoke."

In a later and very important paper, Smithells[1] shows that metallic copper may be isolated from the flame of a Bunsen burner to which a salt of copper had been added. "The effect of introducing a bead of cupric chloride into a Bunsen flame has been carefully described by Lecoq de Boisbaudran.[2] As already stated, he distinguished four cases, but we need only take the first, in which a large quantity of salt is used. The salt first melts, and then in a few moments is seen to be surrounded by a brilliant patch of yellow, like a piece of ordinary candle flame; the exterior parts of this patch are reddish (again resembling carbon luminosity). Outside the yellow a bright blue color appears, and outside this the flame is colored green. The yellow luminosity is of short duration, the blue lasts longer, but soon the only tint remaining is the green.

"These three effects were so local and distinct that it seemed possible to collect the substances to which they were due, and this was done by holding in the flame glass or porcelain basins filled with water. The deposit obtained in this way from the yellow part of the flame was red in color, it transmitted greenish light, it could be burnished, it dissolved in nitric acid with evolution of red fumes, and in fact answered in every respect to metallic copper. The yellow luminosity observed with a large quantity of cupric chloride in a Bunsen flame must, therefore, be attributed to the liberation and incandescence of minute particles of solid copper. The deposit obtained from the blue part of the flame was of a very pale color when freshly formed. On standing, or by breathing upon it, the film absorbed moisture and became quite white; it answered in all its properties to cuprous chloride containing a little of the cupric salt. The green part of the flame produced a deposit which was almost black and corresponded in

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[1] Phil. Mag., [5] 39, 127 (1895).

[2] Spectres lumineux, 156.

appearance and chemical properties to cupric oxide. As the film was very thin, the possibility of it having been originally cuprous oxide and having subsequently oxidized was not excluded.

"From these experiments it is obvious that the three distinct color effects noticeable when cupric chloride is introduced into a Bunsen flame corresponded to three different substances, *viz.*, metallic copper, cuprous chloride, and an oxide of copper. It is highly improbable from a chemical point of view that cupric chloride when introduced into a flame should afford a spectrum. The easy decomposability of this salt and the stability of cuprous chloride (which is volatilizable without change) would lead one to anticipate the decomposition of $CuCl_2$ into Cu_2Cl_2 and Cl_2 long before there could be any question of incandescence. That this is the case can be easily seen by holding a bead of cupric chloride well above the tip of a small Bunsen flame and supporting above it a porcelain basin filled with cold water. Though no flame is seen, the salt melts and volatilizes sufficiently to give a considerable film on the basin, which, on examination, is seen to be almost wholly cuprous chloride....

"The behavior of cupric chloride in the separator admits of easy explanation. In the inner cone the average temperature is extremely high, and the products there generated consist largely of carbon monoxide and free hydrogen. The cupric chloride will therefore not only lose its chlorine but the cuprous chloride, if we suppose it to be formed for a moment, will be immediately attacked by the reducing gases and lose the remainder of its chlorine. We have, therefore, metallic copper, and the average temperature is not sufficient to produce its characteristic spectrum. The copper and the hydrochloric acid resulting from the decomposition of the cupric chloride pass upwards. Some of the former is deposited as a thin metallic film on the inner walls of the outer tube. The rest passes to the outer cone where, at the lower average temperature and in contact with atmospheric oxygen, some cuprous oxide is formed and gives the green tint and oxide spectrum. At the same time some cuprous chloride is formed by the hydrochloric acid, and gives the faint traces of the chloride spectrum."

Quite independently of the work of Smithells, we had come to the conclusion that it was impossible to account for the flame spectra of copper salts without postulating the existence of free copper in some flames. If that were so, it should be possible, theoretically, to precipitate metallic copper on a cold object held in the flame. On trying the experiment it was found to be quite possible to precipitate copper as a thin, bright, metallic mirror from a Bunsen flame into which had been fed the vapors of cupric chloride. This experiment differs in some respects from that of Smithells. The deposit obtained by Smithells was not a bright, metallic mirror, though it could be converted into one by burnishing. It was a red non-reflecting film. We obtained a similar deposit from the yellow portion of the flame and found it to contain copper as Smithells says. It is far from being pure copper, however. It contains a good deal of undissociated copper salt and of red cuprous oxide. Smithells makes no mention of having tried to deposit copper as a practically pure metal from the hottest portion of the flame, whereas our experiments show that the best results are obtained there. It is quite natural that Smithells should not have tried any experiments in the hot portion of the flame because he considered the copper to be set free by reduction and not as the result of a thermal decomposition.

Since it seemed desirable to prove experimentally that other metals could also be precipitated from a flame, the work on the specific reactions taking place in the copper flames was laid aside temporarily and will be reported on in a later paper.

In the experiments on precipitation from flames a Bunsen burner was used for the most part as a source of flame. The burner was arranged to give a large flame and the air supply could be regulated so as to give a quiet-burning flame with maximum heat. In order to protect the flame from any air currents that would interfere with its burning smoothly, the lower portion of the flame was surrounded with an asbestos cylinder about three inches in diameter. A small aperture was cut in this flame protector, through which salts could be introduced into the flame. As a rule, a readily volatilizable salt of each metal was taken because a higher salt concentration is thus obtained in the flame and a higher concentration of free metal in case the flame is hot enough to cause practically complete decomposition of the salt. In most cases the salt was introduced into the flame by means of a platinum wire. This is not an ideal method because there is likely to be local concentration of the salt on one side of the flame and consequently a minimum decomposition. With volatile salts such as stannous chloride and mercuric chloride, it proved advantageous to introduce the vapors into the tube of a Bunsen burner. To do this, a small hole was bored in the tube of the Bunsen burner about two inches from the top. A hard glass tube of small diameter was drawn out to a jet that would fit this hole. Some of the dry salt was placed in the glass tube. The tube was then heated and a very slow current of air passed through it. The fumes of the volatilized salt were thus carried into the burner and up into the flame. This secures a fairly uniform distribution of the salt throughout the flame. It is quite probable that a Gouy sprayer would have been an admirable thing to use with the other salts; but the Gouy sprayer is not in use in the Cornell spectroscopic laboratory and we did not construct one for ourselves until after this work had been finished. A tube of Berlin porcelain about an inch in diameter was found to serve admirably as the cold object on which to precipitate the metal. It was kept cooled by passing a rapid stream of water through it.

The general method of procedure was to get the flame highly colored with the salt; but a large excess of salt is to be avoided, because the undecomposed salt will then precipitate along with the metal and spoil the mirror. In order to get the mirror, the cooled porcelain tube was held for a few seconds in the colored flame, whereupon the film was formed. In so far as the metal is set free by thermal decomposition, one would expect to be able to precipitate metal from any portion of the flame which was sufficiently hot. One would also expect to get the metal with the least contamination by undecomposed salt from the hottest portion of the flame. Both predictions were verified. The tube was therefore held in the hottest part of the flame, about midway between the tips of the inner and the outer cones.

A detailed account will now be given of the separate experiments with copper chloride, cadmium chloride, stannous chloride, mercuric chloride, silver nitrate, lead nitrate, bismuth nitrate, zinc chloride, arsenic trioxide, antimony trichloride, molybdenum oxide, tungstic oxide, phosphorus trichloride, sodium chloride, potassium chloride, and sulphur.

Copper Chloride.—A copper mirror can be obtained equally well by starting with cuprous chloride or anhydrous cupric chloride. The mirror can be obtained smooth, bright, and free from any oxide coating. It is the color of a highly polished piece of copper. Around the mirror there is always some copper oxide, and this substance is obtained almost exclusively from the cooler portions of the flame. The color of the copper oxide is almost black, which can scarcely be due to oxidation of cuprous oxide when the flame is cooled locally by the cold tube, though cuprous oxide is supposed to be the stable oxide at the temperature of the Bunsen flame.

Cadmium Chloride.—The vapors of cadmium chloride decompose readily in the flame and it is a simple matter to obtain a beautiful, bright mirror of metallic cadmium. The cadmium, set free in the flame, burns again to the oxide imparting to the flame the characteristic yellow color which is obtained when cadmium burns in oxygen. If the cold tube is held in the outer edge of the flame, the film obtained consists almost entirely of the brownish black oxide.

Stannous Chloride.—The anhydrous salt decomposes in the flame and a mirror of metallic tin can be deposited from the hottest portion of the flame. This mirror is bright and has the characteristic color of polished tin plate. If the mirror is allowed to get a little too hot, however, it tarnishes and has the familiar reddish tinge. Films can be obtained which contain the brownish stannous oxide and the white stannic oxide in addition to the metal.

Mercuric Chloride.—It was found impossible to get a bright mirror of mercury by condensing the metal on porcelain from a flame containing mercuric chloride. Though the salt is decomposed, the mercury deposits as a dull white film, intermixed with some of the undissociated salt. By means of a platinum wire it was possible to scrape off portions of this white film in such a way as to get fine drops of metallic mercury. The film usually contains some of the black mercurous oxide especially along the edges; but no trace of the red oxide was ever found. In order to get this film at all, it is necessary to have the porcelain tube quite cold and to keep the temperature of the flame somewhat lower than with most of the other metallic salts. The reason for this is the low boiling-point of mercury, which increases the difficulty of condensing the metal from a hot flame.

Silver Nitrate.—When silver nitrate is introduced into the flame, it first melts to a bead and then decomposes. If care be taken, a silver mirror can be obtained, along the edge of which there is precipitated a considerable quantity of black or bluish black silver oxide. If the flame is too hot or if it contains too much salt, spots or specks of metallic silver and also gray, pulverulent silver are obtained instead of a mirror. Since there is a good deal of free silver in the flame when silver nitrate is added, and since silver vapor is blue, it is not impossible that the blue color of the flame is due in part to the vapor of metallic silver.

Lead Nitrate.—When lead nitrate is heated in the Bunsen flame, it decomposes to lead oxide, which latter dissociates in the hottest portion of the flame, thus making it possible for us to obtain a mirror of metallic lead. This mirror is very bright and metallic, but has a characteristic dull blue color. A good deal of undissociated lead oxide precipitates along the edge of the film.

Bismuth Nitrate.—A bismuth mirror was obtained without difficulty from a flame to which bismuth nitrate had been added. This mirror was unusually bright and lustrous. Along the edge of the mirror there precipitated a black oxide,[1] presumably Bi_2O_2. When heated, this oxide changed to the stable yellow Bi_2O_3.

Zinc Chloride.—It is very easy to precipitate metallic zinc from a flame containing zinc chloride. It is somewhat difficult, however, to get a clear untarnished zinc mirror because the zinc tends to precipitate on the tube in a bluish pulverulent form. Using a hot flame and a very slight excess of zinc chloride, it is possible, however, to produce a perfect mirror. The flame has the characteristic blue to bluish green color which is obtained when metallic zinc burns in oxygen.

Arsenic Trioxide.—From a flame, to which arsenic trioxide had been added, there precipitates, on the cold tube, the familiar arsenic mirror which is obtained in the Marsh test for this metal. Only a small amount of the oxide should be added to the flame if a mirror is desired. With more the metal precipitates in a pulverulent form.

Antimony Trichloride.—When antimony trichloride is added to the flame, it is easy to get a mirror like that obtained in the Marsh test. Along the edge of the mirror the antimony precipitates in the black, pulverulent form. Repeated attempts were made to get the yellow modification of antimony; but all were unsuccessful.

Molybdenum Oxide.—Molybdic acid was added to the Bunsen flame and to the hydrogen-air flame. In each case

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[1] Watts: "Dictionary of Chemistry," 1, 513.

there precipitated on the porcelain tube an indigo-blue precipitate, which answers the description of molybdenum molybdate familiarly known as "molybdenum blue," "molybdenum indigo" or "blue oxide of molybdenum." Since no free metal was obtained from the hydrogen flame burning in air, molybdic acid was introduced into the oxyhydrogen flame. The temperature of this flame was high enough to decompose the oxide appreciably, as was shown by the fact that a small mirror of metallic molybdenum was obtained when the porcelain tube was held in the flame a short distance above the bead. This mirror was bright and perfect. It was surrounded by a fringe of the previously mentioned molybdenum blue.

The introduction into the oxyhydrogen flame of a substance like molybdic acid presents some difficulties. The following method was used in these experiments: The molybdic acid was dampened slightly so that it could be matted firmly together. A small amount of this material was then placed in a thick-walled glass tube having a 2 mm bore. The tube was placed vertically on a firm surface and the molybdic acid was rammed into the tube by means of a metallic plunger. More of the acid was added and the operation repeated again and again until about a one inch column of molybdic acid had been formed in the tube. The column was then pressed out of the tube until about three-eighths of an inch were exposed; the free end was held to the edge of the flame. The method worked admirably in this specific case and would probably work well in other cases.

Tungsten Oxide.—The canary-yellow tungsten oxide, WO_3, was introduced into the oxyhydrogen flame in precisely the same way as was done with molybdic acid. A bright mirror of metallic tungsten was obtained with a border of the blue oxide.

Phosphorus Trichloride.—A method employed by the toxicologist for the detection of phosphorus is to put in the flame some of the material to be tested. If phosphorus is present it will impart to the flame a faint greenish color, which becomes a decided bright green when the flame is cooled. From analogy with previous experiments[1] it seemed probable that the change in color arising from the cooling of the flame must be connected in some way with the rate of combustion of phosphorus. We ordinarily think of phosphorus as burning with a bright yellow-white flame; but that is a case of very rapid combustion. To determine the color of the light emitted when the rate of combustion is low, phosphorus was burned with an insufficient supply of oxygen. This was done by placing a piece of phosphorus in a porcelain crucible, igniting it, and covering the crucible with a watch glass. As the air in the crucible became poor in oxygen, the bright flame became less bright and flashes of green were seen. Soon the light emitted by the slowly burning phosphorus was entirely green. The amount of oxygen that diffuses in under the watch glass is sufficient to keep the phosphorus burning but is not sufficient to support rapid combustion, and consequently the flame is entirely green.[2] If the watch glass be lifted, the phosphorus burns up brightly again and no green color can be seen. It is very probable that the green color of the cooled flame, which the toxicologist uses as a test for the presence of phosphorus, is due to the relatively slow oxidation of phosphorus. It ought therefore to be possible to precipitate phosphorus from a flame to which a volatile salt of phosphorus had been added. A little phosphorus trichloride was placed in a hard glass tube drawn out to a jet. Hydrogen was passed through the tube and lighted at the jet. When the tube was heated very gently, the trichloride was volatilized sufficiently to be carried into the hydrogen flame. When a cooled tube was held in the flame a dark reddish precipitate of red phosphorus was obtained. When the precipitate was heated in the air to the ignition point

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[1] Wilkinson: Jour. Phys. Chem., 13, 704 (1909).

[2] The green color is therefore not due to the combustion of PH_3 as assumed by K. B. Hofmann: Pogg. Ann., 147, 94 (1872).

in a dark room, flashes of light could be seen clearly as the phosphorus burned.

Sodium Chloride.—Sodium chloride volatilizes at a high temperature without decomposition and is therefore very stable. In the flame it gives rise, however, to the yellow sodium flame and is therefore undoubtedly dissociated. An attempt was therefore made to see whether metallic sodium could be precipitated from the flame in the same way as the other metals. Of course it was not to be expected that the sodium would remain as metal on the porcelain tube and the presence of caustic soda might be due to the precipitation of this salt direct from the flame, especially since Mendeléeff[1] considers that caustic soda is formed when sodium chloride is introduced into the flame. The first experiments were made with a Bunsen flame. The precipitate consists chiefly of undecomposed sodium chloride but is perceptibly alkaline to phenolphthalein, whereas the original sodium chloride was not. Special blank experiments showed that the alkaline reaction was not due to the tube. The experiment was repeated in the hydrogen-air flame and the alkaline reaction was more marked. Since caustic soda is more volatile than sodium chloride, one would expect to get a more alkaline reaction when the tube is held in the outer or cooler portions of the flame if the caustic soda was formed by hydrolysis. The reverse is the case, however, so that it seems probable that there is no appreciable hydrolysis of sodium chloride in the flame and that we are actually precipitating metallic sodium on the tube. Repeated attempts were made to confirm this conclusion and to precipitate sodium on a cooled surface of mercury, in the hope that enough sodium might be obtained so that an evolution of hydrogen could be detected on adding water. No positive results were obtained and consequently it is justifiable for anybody, who so wishes, to disbelieve, for the present, in the precipitation of metallic sodium from the oxyhydrogen flame.

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[1] "The Principles of Chemistry," 1, 563 (1891).

Potassium Chloride.—When potassium chloride is added to the flame of hydrogen burning in air, the precipitate on the porcelain tube gives only the faintest trace of an alkaline reaction when tested with phenolphthalein solution. In an oxyhydrogen flame the precipitate was markedly more alkaline. This experiment proves that potassium chloride requires a higher temperature to decompose it than does sodium chloride. This is what one would expect in case of dissociation into metal and halogen; but there is no apparent reason for such a difference if we are dealing with hydrolysis. In fact an aqueous potassium sulphate solution is distinctly more alkaline than a sodium sulphate solution. These results therefore corroborate the view that sodium and potassium salts in flames differ from zinc and cadmium salts, chiefly in that the metals of the alkalies are very readily oxidized after precipitation.

Sulphur Dioxide.—In the first experiment sulphur dioxide was fed into a Bunsen flame and a deposit was obtained on the cold tube. The deposit was dark-colored and insoluble in water. It dissolved practically completely in carbon bisulphide and evidently consisted of sulphur which had carried down some carbonaceous matter. In order to eliminate the contamination of carbon, sulphur dioxide was next run into a hydrogen-air flame. The precipitate on the cold tube had the familiar yellow color of flowers of sulphur.

In Table I is given a summary of the experimental data.

The results which we have obtained are really an extension of Deville's work with the hot-cold tube, the flame taking the place of the hot tube. At sufficiently high temperatures all exothermal compounds must decompose. It has proved easier to demonstrate this experimentally than people have hitherto supposed. The reducing flame is not essential because we have obtained copper from a separated flame[1] in which the copper salt was introduced into the oxidizing flame and never came into contact with the reducing flame at all.

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[1] Smithells and Ingle: Jour. Chem. Soc., 61, 204 (1892).

TABLE I

Vapors introduced into flame	Flame	Character of metallic deposit
$CuCl_2$	Bunsen	Mirror; red color
$CdCl_3$	Bunsen	Mirror; very bright metallic
$SnCl_2$	Bunsen	Mirror; bright metallic with faint tinge like tarnished tin
$HgCl_2$	Bunsen	No mirror; deposit of particles of mercury mixed with undecomposed salt
$AgNO_3$	Bunsen	Mirror; lustrous white
$Pb(NO_3)_2$	Bunsen	Mirror; bright metallic with a faint tinge of blue
$Bi(NO_3)_3$	Bunsen	Mirror; very bright white metallic
$ZnCl_2$	Bunsen	Mirror; bright metallic
AS_2O_3	Bunsen	Mirror; bright metallic. Also black amorphous powder
$SbCl_3$	Bunsen	Mirror; bright metallic. Also considerable black powder
MoO_3	Oxyhydrogen	Mirror; bright, lustrous, metallic
WoO_3	Oxyhydrogen	Mirror; bright, lustrous, metallic
PCl_3	Hydrogen	Dull reddish phosphorus
NaCl	Hydrogen	Fine particles of Na or NaOH mixed with undecomposed salt
KCl	Oxyhydrogen	Fine particles of K or KOH mixed with undecomposed salt
SO_2	Hydrogen	Yellow flowers of sulphur

Though the thermal dissociation is the important thing, there are other factors to be considered. The presence of a reducing mixture will displace the equilibrium in one direction. Any electrification will have an effect one way or the other. The dissociation may be forced back by the concentration of other substances in the flame gases. A notable instance of this occurs in the hydrogen-chlorine flame, where the dissociation of the chlorides is reduced to a negligible amount in spite of the high temperature.

The general results of this paper are:

(1) While the general consensus of opinion has been that

free metallic vapors existed in flames, there has been a diversity of opinion as to how the metals were set free. There has been no independent proof of the occurrence of free metals in the flames except in two special cases studied by Salet and by Smithells, neither of whom went beyond the single case on which he worked.

(2) At the temperature of the Bunsen flame many metallic salts are dissociated, the metal being set free. At the higher temperature of the oxyhydrogen flame, more salts are decomposed.

(3) The presence of free metallic vapors in a flame can often be shown by condensing the metals on a chilled porcelain tube.

(4) By precipitation from the Bunsen flame it has been possible to prepare metallic mirrors of copper, cadmium, tin, silver, lead, bismuth, zinc, arsenic, and antimony; and to get mercury in the form of drops.

(5) By precipitation from the oxyhydrogen flame it has been possible to prepare metallic mirrors of molybdenum and of tungsten.

(6) Sulphur can be precipitated from the hydrogen-air flame containing sulphur dioxide; it can also be precipitated, contaminated with carbonaceous matter, from a Bunsen flame containing sulphur dioxide.

(7) Red phosphorus can be precipitated from a hydrogen-air flame fed with phosphorus trichloride.

(8) It seems probable that metallic sodium and potassium have been precipitated from oxyhydrogen flames fed with sodium chloride and potassium chloride. Since these metals oxidize at once, the proof as to their precipitation is not conclusive.

(9) These experiments are an extension of Deville's work with the hot-cold tube.

(10) The principle underlying the experimental results is that all exothermal compounds must decompose if heated

hot enough. The reducing action of the flame gases is not essential, though it may at times increase the decomposition.

(11) In the hydrogen-chlorine flame the dissociation of the chlorides is forced back. In consequence of overlooking this fact and other similar ones, people have been led to deny the fundamental part due to the temperature.

(12) When phosphorus burns relatively slowly, the flame is green just as it is when a phosphorus compound is added to a cooled Bunsen flame.

Cornell University

EQUILIBRIUM IN THE SYSTEM: COPPER ACETATE-PYRIDINE

BY J. HOWARD MATHEWS AND ERNEST BADEN BENGER

Foerster,[1] in 1892, observed the formation of two compounds of copper acetate with pyridine of crystallization: $Cu(C_2H_3O_2)_2, 4C_5H_5N$, and $Cu(C_2H_3O_2)_2.C_5H_5N$. Beyond the statement made by Foerster that the first-named compound decomposes with evolution of pyridine at ordinary temperatures, and that the second is stable at the boiling point of water, we have no data concerning their phase relations. As these are the only compounds of copper acetate and pyridine to be found described in the literature, and as their study was so incomplete, it seemed desirable to determine the ranges of their stable existence and the equilibrium conditions of their solutions in pyridine.

Materials.—The pyridine used was obtained from Merck and was represented to be of the highest purity. It was allowed to stand (with frequent shakings) over sticks of pure potassium hydroxide for two days, then for fifteen hours over barium oxide and potassium permanganate, after which it was digested under a reflux condenser for four hours and finally distilled.[2] The fraction passing over between 115° and 116° at 740 mm was the only portion of the distillate used.

The copper acetate was a "C. P." sample from Kahlbaum. Its water of crystallization was eliminated by the following method: Pyridine was added in excess to the finely powdered acetate, to form $Cu(C_2H_3O_2)_2.4C_5H_5N$. The mixture, after standing for an hour with frequent stirring, was filtered on a Büchner filter, washed three times with pyridine, pressed out with filter paper, recrystallized from boiling pyridine, pressed out with filter paper a second time, washed with pyridine on a Büchner filter and finally given as thorough a

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[1] Ber. chem. Ges. Berlin, 25, 3416 (1892).

[2] Cf. Wilcox, Jour. Phys. Chem., 14, 583 (1910).

drying as possible by pressing out with filter paper, after which it was preserved in tightly closed, glass-stoppered bottles. In this way a product was secured which contained no water.

Thermometers.—For the range of temperature 13° to 95°, a "Normal" thermometer graduated in tenths and capable of being read to hundredths of a degree was used. For lower temperatures a toluene thermometer graduated in degrees and capable of being read accurately to tenths served. Both thermometers were standardized against thermometers which had been standardized by the U. S. Bureau of Standards, and the proper corrections were applied.

Method.—The solubility apparatus was essentially that proposed by Meyerhoffer and Saunders,[1] with glass stirrer (with mercury seal), and was immersed in a suitable thermostat. The temperature of this bath was controlled by an ordinary toluene gas-regulator, which gave a satisfactory constancy of temperature, the maximum variation being 0.1°, except at 95° where it was 0.2°. Above 60° a layer of paraffin aided greatly in maintaining constant temperature, by preventing excessive evaporation. Between 0° and 30° a

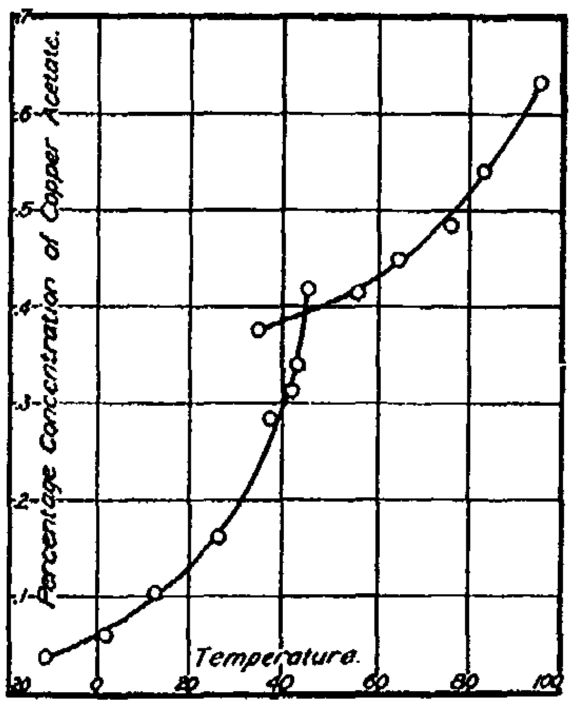

Fig. 1

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[1] Zeit. phys. Chem., 28, 464 (1899).

coil of lead pipe conducting a stream of ice-water was immersed in the thermostat to assist in the regulation of temperature. For the temperature of 0° very finely cracked ice was used, the stirring (which must be very thorough) being done by hand. Below 0° mixtures of ice and common salt and of ice and calcium chloride were used, the thermostat being here replaced by a large silvered Dewar tube. The maximum variation of temperature for these lower temperatures was 0.5°, but for the half hour immediately preceding sampling the variation was less than 0.2°.

The samples for analysis were taken by the apparatus devised by Walton, and Judd[1] in this laboratory. Two samples were always taken at varying intervals of time to insure that equilibrium had been attained. Considerable time was saved by raising the temperature considerably above the point desired, holding it there for half an hour, and then lowering it.

The analyses of the samples were carried out by a method devised by Mr. Samuel Spero in this laboratory. The sample was washed out of the weighing tube with water and evaporated to dryness on the water-bath, after which the least amount of concentrated nitric acid which would dissolve all the solid was added, the solution diluted to 200 cc. and heated nearly to boiling. The copper was precipitated with potassium hydroxide, the liquid poured off through a filter, the precipitate washed once with hot water by decantation, dissolved in the dish with concentrated nitric acid and the resulting solution passed through the filter and caught in a weighed platinum dish. The copper was deposited from this nitric acid solution in the usual manner, using a rotating anode and N. $D._{100}$ 0.6 to 1.0 ampere.

The data obtained are given in the following table:

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[1] Jour. Am. Chem. Soc., 33, 1039 (1911).

Temperature	Weight of sample	Weight of copper deposited	Percentage of copper acetate in sample	Average
95.40°	2.5026	0.0554	6.32	6.31
	2.8660	0.0631	6.29	
83.30	2.6971	0.0520	5.51	5.40
	2.4592	0.0459	5.33	
76.20	3.3334	0.0561	4.81	4.83
	3.2780	0.0555	4.84	
64.30	3.3814	0.0522	4.41	4.48
	3.0133	0.0479	4.54	
55.70	3.6564	0.0539	4.21	4.13
	3.4207	0.0483	4.04	
45.20	3.8082	0.0556	4.17	4.17
	3.3851	0.0495	4.17	
43.20	2.8901	0.0342	3.38	3.39
	2.7686	0.0330	3.40	
41.90	3.4541	0.0374	3.09	3.12
	3.6924	0.0407	3.15	
37.40	2.7579	0.0273	2.83	2.83
	2.9022	0.0287	2.83	
34.80	3.5853	0.0473	3.77	3.75
	3.3975	0.0442	3.72	
26.45	2.8403	0.0161	1.62	1.61
	3.0405	0.0169	1.59	
13.00	3.7502	0.0131	1.00	1.03
	3.3487	0.0125	1.06	
2.00	2.3517	0.0052	0.63	0.60
	3.3711	0.0067	0.57	
—11.60	3.7070	0.0047	0.36	0.37
	3.2101	0.0043	0.38	

The Solid Phases.—The analyses of the solid phases were made in much the same way as the analyses of the samples from the solubility tube. The blue compound, $Cu(C_2H_3O_2)_2 \cdot 4C_5H_5N$, which is in equilibrium under the conditions represented by the lower branch of the curve, was found by analysis to contain 12.55 percent of copper, corresponding to the formula as stated above, in which the theoretical percentage of copper is 12.78. The discrepancy was undoubtedly due to imperfect drying, as the crystals appeared moist. It was found impossible to dry them thoroughly without decomposition, *i. e.*, loss of pyridine of crystallization. Since this compound had been described by Foerster no ultimate analysis was considered necessary.

The green compound $Cu(C_2H_3O_2)_2.C_5H_5N$, which is in equilibrium with the solution under conditions represented by the upper branch of the curve, was found to contain an amount of copper corresponding to the formula as stated. Since this compound has also been described by Foerster no ultimate analysis was made.

Inspection of the curve shows the transition point of the two salts to be 44.7°. This temperature is very certain as points for each salt were obtained in the meta-stable condition, making extrapolation unnecessary.

Foerster's conclusion that no compound intermediate between the compounds $Cu(C_2H_3O_2)_2.4C_5H_5N$ and $Cu(C_2H_3O_2)_2.C_5H_5N$ is formed has been verified, and the range of stable existence of these compounds has been studied for the temperature interval —11.6° to 95°.

Laboratory of Physical Chemistry
University of Wisconsin
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MERCURIC OXIDE JELLIES

BY E. H. BUNCE

This work was chiefly a repetition of that by J. Emerson Reynolds.[1]

"When a solution of mercuric chloride is added slowly to a mixture of acetone with a dilute aqueous solution of potassium hydrate, the mercuric oxide first precipitated is dissolved, with the production of a clear colorless liquid. The addition of the mercurial solution can be continued until a white precipitate makes its appearance, the alkali being still in excess.[2] If the solution be filtered at this point, an apparently opalescent, yellowish colored liquid is obtained.[3] If one portion of this alkaline solution be boiled for a few minutes, a thick gelatinous mass suddenly separates, and further ebullition is rendered difficult, if not impossible. Another portion of the liquid gelatinizes when treated with an acid in slight excess; and, if the original solution be moderately strong, the vessel in which the experiment is made may be inverted without risk of spilling its contents. Finally, if some of the mercuric solution be exposed over sulphuric acid *in vacuo*, it leaves on partial evaporation a gelatinous mass, on the surface of which latter crystals of potassium chloride soon make their appearance. When the desiccation is complete, a yellowish resinoid body is obtained, together with a large quantity of very beautiful acicular crystals of

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[1] Proc. Roy. Soc., 19, 431 (1871).

[2] The same results can be obtained when mercuric oxide is precipitated from any of its salts, washed rapidly, and then digested with excess of acetone and potassium hydrate. The best mode of operating, however, is that stated in the text.

[3] The different solutions exhibit a slight opalescence, not completely removable by ordinary filtration. This opalescence appears to be due to the very gradual separation, at ordinary temperatures, of traces of the same anhydrous substance which is thrown down very rapidly at a boiling heat. In composition the latter body is identical with the anhydride obtained by other methods and described further on.

the chloride and a certain amount of potassium carbonate. The solution of mercuric oxide in potassium hydrate in presence of acetone takes place as easily in alcoholic as in aqueous liquids.

"Preliminary experiments similar to the foregoing were sufficient to indicate that the chief compound produced in the reaction above referred to might be regarded as a colloid body. I, therefore, took advantage of the late Professor Graham's beautiful dialytic method[1] for effecting its purification from crystalloids and have met with complete success.

"As the preparation of a *strong* solution of the pure acetone mercuric compound suitable for dialysis is attended with some difficulty, I may now describe in detail the mode of operating proved by experience to afford the most satisfactory results. Forty grams of pure mercuric chloride are to be dissolved in about 500 cc of hot water and the solution then allowed to cool, even though crystals of the salt separate. Twenty-nine grams of potassium hydrate are next dissolved in about 300 cc of water: 15–20 cc of acetone should now be placed in a capacious glass balloon, and diluted with 250 cc of water. The reaction is then to be managed as follows: about 150 cc of the alkaline solution should be added to the aqueous acetone, and then 250 cc of the mercuric chloride poured in. Resolution of the mercuric oxide first thrown down proceeds slowly at the outset, if the mixture be not warmed. After a time the oxide redissolves quickly, if the contents of the balloon are agitated briskly. When the first half of the mercuric solution has been added, the remaining 150 cc of potassium hydrate are to be poured in cautiously and the residual mercuric chloride then mixed, with the precautions already stated.

"The solution prepared in the manner described is usually turbid, but can easily be filtered clear from the small amount of mechanically suspended matter. The filtrate should next be placed on a large hoop dialyzer, covered as usual with care-

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[1] "Liquid Diffusion Applied to Analysis," Phil. Trans., 151, 183 (1861).

fully prepared parchment-paper, and the vessel floated on a considerable volume of distilled water. After two days action the diffusate will be found to contain a large quantity of potassium chloride, some potassium hydrate and but a very small amount of mercury. The process of diffusion is to be continued, the diffusate being replaced by pure water twice each day, until the liquid on which the analyzer floats no longer affords a cloud when treated with a solution of silver nitrate. The process may then be considered terminated, and the pure colloidal liquid obtained. The contents of the dialyzer can now be removed, and should be free from all odor of acetone. A few drops, when evaporated to dryness on platinum-foil and the residue ignited, should volatilize completely.

"The mode of operating just described affords the strongest colloidal liquid that can conveniently be prepared directly in the pure state; but where degree of concentration is of no importance, I find that it is better to dilute the alkaline mercurial solution with its own volume of pure water just before dialyzing."

Reynolds evaporated the carefully prepared colloid liquid to dryness; the resinoid residue was powdered very finely and dried carefully. The composition of the substance could be represented satisfactorily by the formula $(CH_3COCH_3)_2$-Hg_3O_3 and Reynolds assumed that the substance was a definite chemical compound. While this may be true, the evidence would not nowadays be considered as conclusive. Reynolds has the following to say in regard to the properties of the alleged compound: "Analogy would lead us to conclude that the colloid liquid obtained by dialysis is a hydrate of the body represented by the above formula ($(CH_3COCH_3)_2$-Hg_3O_3); but since evaporation *in vacuo* is sufficient to remove the water completely, the hydrate can possess but little stability. Properly speaking, this hydrate is no doubt a true liquid, and as such is miscible with other liquids. The reaction of this hydrate is neutral to test-papers.

"When the aceto-mercuric hydrate contains five percent of the anhydrous compound, it will, if quite pure, remain liquid for twelve or fourteen days, toward the end of this time becoming gradually less fluid, until the whole 'sets' to a firm jelly. The same result may be brought about in a few seconds by the addition to the perfectly neutral liquid of very minute quantities of any of the following substances: hydrochloric, acetic, nitric, sulphuric (incompletely), chromic, oxalic, tartaric, or citric acids; by potassium, sodium, ammonium, barium and calcium hydrates; by calcium chloride, mercuric chloride, sodium acetate, and other neutral salts. Contact with certain insoluble powders, such as calcium carbonate, and even alumina, induces pectization.[1]

"Elevation of temperature quickly determines the gelatination of the liquid. If containing five percent of the ketone compound, a very firm jelly is produced on heating to 50° C. In one experiment, a quantity of the liquid was taken and some bright, carefully-cleaned copper gauze introduced. The liquid did not pectize, nor did any trace of mercury deposit on the copper, after standing for a day. The temperature of the whole was then raised to 50° C.; a transparent jelly was at once produced, of such strength that the vessel in which it was contained could be inverted without any risk of loss. This jelly, enclosing the bright copper gauze, has remained in my possession for eight months without giving the slightest indications of a disposition to change.

"Small zoological specimens, when inclosed in the same way in a jelly of the mercuric ketone compound, were found to keep well when carefully cleansed before they were sealed up in the gelatinous envelope.

"By evaporation, a liquid containing eight percent of the ketone compound was obtained, but it pectized in a few hours.

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[1] In accordance with the nomenclature of Professor Graham, we must call the liquid colloid hydrate the "hydrosol" of the new compound, the gelatinous hydrate the "hydrogel" and the change from the former to the latter "pectization."

A two percent hydrate retained its liquidity for several months. Once a jelly formed in any of these liquids, I have not succeeded completely in reconverting it to the liquid state by very cautious treatment with potassium hydrate, even when aided by diffusion.

"The *alcosol* of the mercuric ketone compound was obtained by the method adopted by Professor Graham in preparing the corresponding silicic alcoholate—that is to say, by adding to a one percent hydrate an equal volume of alcohol, and exposing the mixture over quicklime until most of the water was removed: the alcohol remained. This liquid could be boiled without pectizing; but if the ebullition continued for some time, a jelly was suddenly obtained. This insoluble jelly corresponded to that produced on heating the hydrate, or adding to it any of the bodies capable of pectizing it; in the former case alcohol, and in the latter water, being associated or united with the mercuric ketone compound.

"It has now been shown that the new body is capable of affording *hydrosol* and *hydrogel*, and *alcosol* and *alcogel*; it must, therefore, be regarded as a very strongly marked member of Professor Graham's group of these colloids, though chemically differing widely from previously described compounds of this class.

"When the colloid hydrate was treated with sulphuretted hydrogen, mercuric sulphide was produced. The liquid filtered from the sulphide yielded *acetone* on distillation. Digestion with dilute hydrochloric acid likewise effected the decomposition of the colloid body, mercuric chloride being produced and acetone liberated. Nitric and sulphuric acids, when dilute, did not decompose the compound with the same facility as hydrochloric acid. Treatment of the hydrosol with copper, zinc, or iron *at ordinary temperatures,* failed to effect the substitution of either metal for the mercury in the compound. Prolonged contact with each of the two last-mentioned metals caused pectization, the metal subsequently becoming encrusted with a white substance. Heat produced the same result more rapidly."

At first I repeated Reynolds' experiments exactly but I soon found that the process could be simplified if one was interested chiefly in making a jelly. The easiest method is to dissolve 30 grams KOH and 20 cc acetone in 500 cc water and to add slowly a saturated solution of mercuric chloride, shaking the mixture continually until the first faint, permanent precipitate appears. A precipitate appears on adding the mercuric chloride but disappears on shaking until a certain amount of mercuric chloride has been added, after which either a white flocculent or a fine, yellow, granular precipitate is formed. The solution jells on standing exposed to the air for a length of time depending on the concentration of the mercuric chloride. The solution may also be made to jell by desiccation over sulphuric acid, by addition of a small amount of an acid, or by heating; but too much heating causes the precipitation of a fine granular precipitate and the solution then does not jell. It is important to use a sample of mercuric chloride containing no mercurous chloride. Since mercurous chloride is by no means an unknown impurity in this case, it is much wiser to recrystallize the mercuric chloride from water.

The first experiments concerned the variation in the amount of mercuric chloride. To each beaker were added 40 cc KOH and acetone solution, and then a definite amount of a saturated solution of mercuric chloride. The beakers were allowed to stand for three days and were then examined. The beakers containing 1–15 cc mercuric chloride solution did not jell at all. There was a black precipitate in the bottom of each beaker and a clear, yellowish liquid above. With 20 cc $HgCl_2$ solution, the solution becomes opalescent and there is a heavy granular precipitate. With 30 cc $HgCl_2$ solution there is formed a soft jelly with a thin layer of liquid on top. With 50 cc the solution jelled after standing several hours; at first there was a thin layer of liquid on top of the jelly but this disappeared in time. With 60–90 cc mercuric chloride solution a firm jelly was obtained in a short time. With

100 cc $HgCl_2$ a jelly is formed with a permanent supernatant liquid layer. It is thus clear that a good jelly is obtained only between certain limits for the mercuric chloride. If left standing for a long time, these jellies dry out and contract, shrinking away from the glass walls of the beaker and cracking. They still remain moist for a long time; but finally dry down to little heaps of powder. The jellies are a pure white color and feel like salve when rubbed between the fingers. They are alkaline to litmus paper. One sample of jelly was sealed in an air-tight dish to prevent loss of moisture. At the end of three months the jelly was apparently entirely unchanged.

In another run I made up mixtures containing 40 cc KOH and acetone solution and 50 cc saturated $HgCl_2$ solution. To these were added two-gram lots of different salts. With potassium sulphate, and sodium nitrate, no immediate effect could be noticed, the solutions apparently giving as good jellies as though the salts had not been added. Of course, the salts crystallized in case the jellies were left standing a long time in the air. With sodium acetate a jelly-like structure was obtained; but no real jelly. Addition of potassium carbonate gave rise to a thick, viscous, milky liquid while addition of cobalt sulphate or copper nitrate caused the formation of a granular precipitate.

In the next set of runs 80 cc $HgCl_2$ solution were added to 40 cc KOH and acetone solution. The mixtures were heated for varying times and consequently to varying temperatures, so as to bring out the effect of heating. The ordinary temperature was 20°. When not treated at all, the mixture was an amber-colored solution which formed a good jelly on standing. When the solution was heated for one minute (to 30°) it jelled more rapidly than the unheated solution. On heating two minutes (to 39°), the solution became cloudy, then separating into a good jelly at the bottom and a yellow liquid above. In time the solution dried to a firm jelly with no upper liquid layer. The same thing happened when the solution was heated three minutes (to 60°), or four minutes (to 63°). When heated five minutes (to 69°) a white, cloudy precipitate formed which became granular and settled to the bottom. Though a jelly was formed, it was not a good one. When the solution was heated longer, a granular precipitate settled and no jelly was formed. It is not solely a question of evaporation because one mixture was placed in a flask fitted with a reflux condenser and was boiled for eight hours. A granular precipitate settled and no jelly was formed. If the mixture is placed in a stoppered bottle at room temperature, a jelly is formed with a liquid layer on top, showing that evaporation is necessary in order to get a firm homogeneous jelly when starting with these solutions. If time had permitted I should have liked to try varying the relative amounts of caustic potash and acetone, and the absolute amounts of water.

The jellies do not dissolve in water even though the water be boiled for several hours. They break down, however, into a granular precipitate. If a few drops of concentrated hydrochloric acid or nitric acid be added to the water, the jellies dissolve readily to a clear solution when heated. If this solution is cooled and then made alkaline either with KOH or with the KOH and acetone solution, no jelly is obtained and the precipitate contains a good deal of black mercurous oxide. I did not have time to find out when or how the reduction to mercurous salt took place. Since it has seemed impossible to get a jelly when the mercuric chloride contains mercurous salt originally, it is possible, though not proved, that the mercuric oxide jellies could be made to liquefy and to jell alternately for an indefinite number of times if no reduction to mercurous salt took place.

The general results of this paper are:

1. Reynolds' work on mercuric oxide jellies in presence of acetone has been repeated and confirmed.

2. For given amounts of acetone and caustic potash, the amounts of mercuric chloride can vary only between limits if a good jelly is to be obtained.

3. Addition of potassium sulphate or of sodium nitrate had no apparent effect on the jelling of the mixture; addition of potassium carbonate caused the formation of a viscous milky liquid, while cobalt sulphate or copper nitrate caused the formation of a granular precipitate.

4. A slight rise in temperature causes a mixture to jell more quickly; but heating for five minutes or more at temperatures above 63° seems to prevent the formation of jellies.

5. The effect of heating is primarily a temperature phenomenon and not one of evaporation, for the formation of a jelly is prevented by heating the mixture in a flask fitted with a reflux condenser.

6. When heated with water the mercuric oxide jellies break down to a granular precipitate.

7. When the jellies are heated with water to which a few drops of concentrated hydrochloric acid or nitric acid have been added, no jelly is formed; but we get a granular, black precipitate, which contains mercurous oxide. No jelly is formed when the solution is made alkaline again.

8. It is not known whether it is the mercurous oxide which alone keeps the solution from jelling a second time.

9. The mercuric oxide jellies break away from the glass walls when drying. They also crack, but no second layer of liquid forms.

This investigation was suggested by Professor Bancroft and has been carried out under his supervision.

Cornell University
June, 1913

NEW BOOKS

A Dictionary of Applied Chemistry. *By Sir Edward Thorpe. Vol. V. 17 × 23 cm: pp. v + 830. New York; Longmans, Green, and Co., 1913. Price: $13.50.*—The fifth and last volume covers the ground from sodium to zymurgy. Among the interesting subjects in this volume are: sodium; soils; solders; solubility and solution; specific gravity; spectrum analysis; starch; steam; strontium; sublimation; sugar; sulphide dyes; sulphur and sulphuric acid; synthetic drugs; tannins; tartaric acid; tellurium; terpenes; thallium; thermometers; thermostats; thorium; tin; titanium; tobacco; toxins and antitoxins; triphenyl methane coloring matters; tungsten; ultramarine; uranium; urea; vanadium; varnish; vat dyes; vegeto-alkaloids; water; waxes; whiskey; wine; destructive distillation of wood; wool; zinc.

The first volume appeared in 1912 and the last one at the very end of 1913, an interval of less than two years. This is a record of which both the editor and the publishers may well be proud. It is a difficult enough matter to get a few men to turn in manuscript anywhere near the time for which it has been promised. To get dozens of people to do this simultaneously would seem an impossible feat, except that the editor has accomplished it. The quality of the work is also of the highest grade. It has been a source of admiration to the reviewer to see how complete the more important articles were, in spite of the fact that an enormous number of subjects has been treated in a relatively limited space. The one serious defect in the dictionary is that the literature references are unreliable. The five volumes are invaluable as reference books and should be in every chemical library. *Wilder D. Bancroft*

Handbuch der Mineralchemie. *By C. Doelter. Vol. II. Parts I-IV. 18 × 25 cm: pp. 160 (each part). Dresden: Theodor Steinkopff, 1913. Price: 6.50 marks (each part).*—These four numbers of the second volume deal with: silicic acid in the forms of quartz, chalcedony, and opal; agates; the lithium, sodium, potassium, and magnesium silicates; talc, meerschaum, and serpentine; calcium silicate and the double silicates of calcium with sodium, magnesium and iron, including the pyroxenes and amphiboles, asbestos and hornblende.

The problems of the silicates and of silicic acid can be solved only by people who have a thorough working knowledge of physical chemistry and of colloid chemistry. The editor and his collaborators are not fortunate in this respect, with the result that the problem is presented in a very confused way. On p. 73 Doelter seems to believe that all compounds are stable at their melting-point; and the possibility of there ever being more than two series of solid solutions has evidently never occurred to him. On p. 117 he commits himself to the opinion that inversion points are of no importance because the changes at them do not take place instantaneously. While Doelter is quite clear on p. 74 that the zeolites do not form definite hydrates, on p. 75 he accepts Tschermak's view that they probably do. Tschermak bases his conclusions on experiments on the rate of hydration, pp. 93, 228 and 234, although he ought to know that these cannot compare in accuracy with experiments on equilibrium relations. It is quite on a par with the view that silicates do not have definite melting-points merely because these are extraordinarily difficult to determine accurately. Doelter also seems to believe that all colloidal precipitates must be definite compounds because it is possible to obtain definite crystalline compounds as colloidal precipitates, p. 85. Because it is possible to prepare colloidal barium sulphate we must therefore conclude that the so-called aluminum silicates are necessarily definite compounds. It is quite clear that Doelter has never understood van Bemmelen's work and it really seems as though Doelter has no definite theoretical beliefs by which he is willing to stand when the facts seem to go against him. One cannot help feeling sorry for a man who has never had the satisfaction of being able to predict that such and such experimental results must be wrong regardless of their apparent accuracy.

There are some interesting facts in regard to mineralizers, pp. 52, 145, 154. Carbonates, borates, fluorides and tungstates are said to be the most efficient mineralizers. Doelter considers that they do not act like catalytic agents; but that they displace the equilibrium. In so far as what separates is a form of pure SiO_2, the presence of substances in the melt cannot possibly affect the real equilibrium, though these substances may have an enormous effect on the ease of obtaining a given form. Doelter seems to make the tacit assumption that whatever form crystallizes is necessarily the stable form.

It is interesting to note that the water in the zeolites can be replaced by alcohol, carbon bisulphide or benzene, p. 74, and that the zeolites can also take up mercury, calomel, bromine or iodine, p. 71. On p. 184 there is an account of the artificial staining of chalcedony. Red is obtained with iron oxide, green with chromium, yellow with hydrochloric acid, and black with sugar and oil of vitriol. Meerschaum can also be stained with fuchsine or with acid violet, p. 381.

The fourth number appeals the least to the physical chemist, the most important subject from his point of view being asbestos. Fersmann distinguishes two groups of asbestos, one with parallel fibres and one with crumpled fibres. No special reason is given for this differentiation and no explanation is offered for the occurrence of the crumpled fibres.

This volume is a treasure-house of observations and as such is extremely valuable. It is also valuable in showing how far we still are from anything that might be called a scientific treatment of silicic acid and the silicates. The problems are really for the colloid chemist who has not as yet risen to the situation.

Wilder D. Bancroft

Geschichte der deutschen Naturphilosophie. *By Carl Siegel. 16 × 24 cm; pp. v + 390. Leipzig: Akademische Verlagsgesellschaft, 1913. Price: 10 marks.* Though Ostwald disclaims any connection between his point of view and the philosophy of Schelling, the author prefers to consider the first as a development of the second. This is chiefly a question of definition. The oxygen theory of combustion was absolutely the opposite of the phlogiston theory and yet it grew out of it in the sense that it was developed in consequence of the shortcomings of the phlogiston theory becoming too obvious. The author begins his historical sketch with a chapter on German metaphysics before Leibnitz. After this comes a chapter on Leibnitz and one on Kant and Fries. The views of Herder, Goethe, Schelling, and Schopenhauer are treated under the heading of the romantic school, while a chapter on Herbart and Feuerbach gives the needed contrast. Lotze and Fechner are considered as the forerunners of the modern school, of which Mach and Ostwald are the leaders. The author considers the views of Ostwald as being a modernized version of those of Leibnitz or perhaps it would be more accurate to say that both philosophies have a common goal.

Wilder D. Bancroft

The Preparation of Organic Compounds. *By E. DeBarry Barnett. 14 × 21 cm; pp. v + 301. Philadelphia: P. Blakiston's Son and Co., 1912. Price: $2.75.*—"In the present volume the author has aimed at giving a general outline of the methods actually employed in preparing organic compounds, and thus providing not only a laboratory manual, but also a book which may be used as a companion volume to the usual theoretical text-books.

"In the first chapter will be found a short description of the most common apparatus and reagents used in preparative organic work; and although some of the apparatus described may be regarded as rather crude for academic practice, it must be borne in mind that the average works laboratory, at all events in this country, is not fitted with all the latest refinements, and that one of the chief difficulties experienced by the young chemist on first entering works is to adapt himself to his environment. Although to some minds the idea of carrying out chemical preparations in sauce-pans, jam-pots, etc., may seem rather bizarre, experience will show that such apparatus is quite as satisfactory and considerably less expensive than the more conventional and more brittle beakers and basins.

"The description of the processes given is less full than in most books on organic preparations, but the details are sufficient to enable the average student to carry out the preparations successfully, without being so exhaustive as to reduce his work to mere mechanical routine. The book is not intended for those who are endeavoring to study chemistry by correspondence lessons, and those working in a university or technical college laboratory can usually refer to a senior student or to a member of the staff when in difficulties."

The chapters are entitled: apparatus, methods of manipulation, reagents; the hydrocarbons; the halogen compounds; the alcohols, phenols, and mercaptans; the aldehydes, ketones, quinones (and quinone-imides) and some derivatives of the same; the ethers and sulphides; the carboxylic acids, their anhydrides and esters; the nitriles or cyanides; the nitroso- (and *iso*-nitroso-) and nitro-compounds; the amino-compounds; the diazo-, diazoamino-, diazoimino-, azo-, azoxy-, and hydrazo-compounds; the sulphinic and sulphonic acids; miscellaneous types.

The author covers a great deal more ground than is usually the case. In only a limited number of cases is there anything about yields and there is practically nothing about conditions. The book is therefore one of the orthodox organic laboratory manuals and does not show any signs of the change of spirit which organic chemistry must undergo before it comes into its own again.

Wilder D. Bancroft

FLAME REACTIONS. II

BY WILDER D. BANCROFT AND HARRY B. WEISER

The Luminescence of Heated Gases

As far back as 1792 Thomas Wedgwood[1] showed that heated air is not luminous. "An earthenware pipe, of a zig-zag form, was placed in a crucible, which was filled with sand, the two open ends of the pipe being left uncovered; one of them was of a proper form for receiving the nozzle of a bellows, the other bent into angles of the form of the letter Z; on this last was fastened a globular vessel with a lateral bent pipe to let out air but exclude all external light, and with a neck in which was inserted a circular plate of glass. The crucible with the sand and the part of the pipe contained in it was then heated to redness. Having my eye fixed on the neck of the vessel, and observing it perfectly dark within, I directed an assistant to blow with the bellows. The stream of air, sent through the red-hot tube, not being at all luminous, I fixed a small strip of gold in the orifice of the tube, which, after two or three blasts, became faintly red; thus proving that the air, though not luminous, was equal in temperature to what is usually called red heat. I then heated the crucible to a brighter redness; the stream of air, blown through the bright red-hot tube, still came out perfectly dark, but the strip of gold, exposed to it, shone both *sooner* and *brighter* than before."

Ever since this time there has been a difference of opinion as to the extent to which the luminescence of a heated gas is purely a question of temperature or is the result of chemical action. Melloni[2] considers that chemical action plays an important part. "When one body combines chemically with another, its molecules acquire in an instant a very violent vibratory motion, and then may subsequently assume vibra-

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[1] Phil. Trans., 82, 272 (1792).

[2] Phil. Mag., [3] 32, 275 (1848).

tions that are slower. This is what appears to take place in flames, which originate in the combustion of bodies; they commence almost always by a blue or violet light, and then become white or yellow." Dibbitts[1] lays stress on the emission of a heated gas. "When two gases combine chemically, giving rise to a flame, there are several possible causes for the emission of light. We will illustrate this by a concrete example. When hydrogen burns in chlorine, we get a green flame which gives a continuous spectrum without lines. This light may be due: (*a*) to the heated hydrogen; (*b*) to the heated chlorine; (*c*) to the heated hydrochloric acid; (*d*) to a heated substance which exists only temporarily as an intermediate compound; (*e*) to the chemical reaction itself. Let us consider for a moment these five cases which are the only conceivable ones.

"We are not dealing with (*a*) because Plücker has shown that highly heated hydrogen gives a spectrum consisting of three bright lines;[2] nor with (*b*) because Plücker has shown that highly heated chlorine gives a spectrum with characteristic bright lines. Case (*d*) is improbable because the simplest way in which hydrogen and chlorine can react is in equal volumes, in other words, to form hydrochloric acid; it is very unlikely that a more complex substance would exist in the flame as an intermediate step in the formation of hydrochloric acid.[3] This leaves only (*c*) and (*e*). The following experiment is intended to distinguish between these two possibilities: A mixture of hydrogen and hydrochloric acid was burned in air or in oxygen, which is the same as feeding hydrochloric acid into a flame of hydrogen burning in oxygen. If (*c*) is right we should get the same light as when hydrogen burns in chlorine because we have hydrochloric acid which is

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[1] Pogg. Ann., 122, 539 (1864).

[2] [What Plücker really studied was the spectrum given when an electric discharge passes through a Geissler tube containing hydrogen. He assumed that this was the spectrum of highly heated hydrogen.]

[3] [This reasoning is not conclusive. One might have an addition compound, $H_2.Cl_2$, analogous to the chlorine addition compounds of chlorine with benzene.]

merely being heated very hot. If (*e*) is correct, we should get nothing but the light emitted by a flame of hydrogen burning in oxygen, because the hydrogen and chlorine have already combined and *this* chemical reaction[1] cannot therefore give rise to light.

"The experiment is in favor of (*c*) because we get the same light and the same spectrum as when hydrogen burns in chlorine. It is thus proved that, in this case at any rate, the light is *not* due directly to the chemical reaction but is due to the heating of the products of combustion. The burning of hydrogen and carbon dioxide or hydrogen and sulphur dioxide may be used to illustrate the same conclusion. When a mixture of hydrogen and carbon dioxide burns, a blue flame is obtained giving a continuous spectrum which is not that of hydrogen, of carbon, of oxygen, or of water. There are two possibilities. Hydrogen and carbon dioxide may react to form water and carbon monoxide, the latter reacting with oxygen from outside and *this chemical reaction giving rise to the blue light;* or hydrogen may react with oxygen from outside and the resulting flame may heat the carbon dioxide so much that *it becomes self-luminous and emits the blue* light. The experiments do not enable one to decide definitely between these two alternatives. From the analogy with the preceding experiment (flame of hydrogen and hydrochloric acid), we may conclude that the heated product of combustion (CO_2) is the cause of the light and *not* the chemical action.

"Quite in accord with this is the experiment in which a mixture of hydrogen and sulphur dioxide are burned. The experiment proves nothing; but can easily be accounted for on the assumption that *no* light is emitted as the direct result of the chemical action but that all the light is due in this case chiefly to the highly heated sulphur dioxide. According to this hypothesis highly heated sulphur dioxide gives a spectrum

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[1] [The author of course does not consider the possibility of hydrochloric acid dissociating.]

which has been described under the sulphur flame. In the flames of burning sulphur or hydrogen sulphide we have highly heated sulphur dioxide and it gives the same spectrum. In the carbon bisulphide flame we have highly heated sulphur dioxide and carbon dioxide; this shows the light due to both. In the flame of burning carbon monoxide it is the highly heated carbon dioxide alone which emits the blue light; and in the oxyhydrogen flame it is the highly heated water vapor which emits the faint light peculiar to this flame."

Hittorf[1] is distinctly on the other side. "All solids probably cease to phosphoresce at the temperature at which they begin to emit red light, at the so-called dull red heat. The ordinary non-metallic gases behave quite differently. The spectra of the first order are obtained at low temperature when an electrical current passes and are also given by many gases when burned in oxygen. The light of our ordinary flames, which contain no solid particles, is not due to the temperature but is caused by the chemical reaction and should be considered as phosphorescence. For, if the same gases are raised to the temperature of the flame without any chemical reaction taking place, they emit no light which can be detected by the eye. It is easy enough to convince oneself of this by suspending horizontally in the hottest portion of the Bunsen flame a narrow cylindrical tube of the thinnest possible platinum foil. To prevent one's eyes being dazzled by the light radiated by the glowing metal, it is necessary to look through a narrow tube along the axis of the cylinder. If the room is dark, the gas inside the tube will appear dark and quite different from the gases of the luminous flame. The same result is obtained if one looks at the air inside a tube which has been heated white-hot in a coal fire.

"A later paragraph will also show that the electrical behavior of the flame gases is quite different from that which the same gases show at the same temperature when no chemical reactions are taking place.

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[1] Wied. Ann., 7, 587 (1879); 19, 73 (1883).

"These facts do not conflict with the law that all substances begin to emit light of the same wave-length at the same temperature. At these temperatures the ordinary gases show practically no absorption and consequently Kirchhoff's law requires that they shall also show no emission."

Siemens[1] came to much the same conclusions independently of Wedgwood and of Hittorf. "When gases burn with a brilliantly luminous flame, the light is well known to be a secondary phenomenon due to the solid or liquid particles in the flame being heated until they glow. Gases, which give rise to no solid or liquid particles, burn with a relatively feebly luminous flame which is usually bluish, though the color varies somewhat with the nature of the gas. People are wont to account for this luminosity by saying that the highly heated gases themselves emit light. So far as I know no experiments have ever been published to show whether pure gases really emit light when heated. Some considerations as to the emission of light by the sun....and some casual observations made it seem to me improbable that heated gases emit light and I therefore decided to make some experiments in regard to this. If the experiments were to be conclusive, they must be made at temperatures higher than those reached in the luminous combustion. I soon convinced myself that, for this and other reasons, laboratory experiments would not give a satisfactory result. My brother, Friedrich Siemens, placed at my disposal in Dresden a regenerative furnace which was used for manufacturing hard glass. The furnace could easily be heated to about 1500°–2000° C which is as high as the specially refractory walls would stand. When these temperatures were reached and when the further flow of gas and air into the furnace was cut off, the hot walls of the furnaces kept the enclosed air for a long time at a very constant temperature. In front of the openings in the furnace there were placed a series of well-blackened screens with a central opening, which permitted one to look through the hot

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[1] Wied. Ann., **18**, 311 (1893).

furnace without any rays from the walls reaching the eye. After the furnace had been made completely tight and the lights had been put out so that there was no external light, it appeared that the highly heated air in the furnace did not emit any light that was visible to the eye.... For the experiment to succeed it was essential that no combustion should be taking place in the furnace and that one should wait until the air in the furnace was as free from dust as possible. Any flame in the furnace, even when apparently not in the line of vision, or the slightest amount of dust caused a glow to be seen.

"These experiments show the erroneousness of the previously held view that highly heated gases are themselves luminous. In the furnace there was air mixed with the products of the previous combustion, in other words, oxygen, nitrogen, carbon dioxide, and water vapor. If any one of these gases were self-luminous, the field of vision would have appeared bright. If the gases are not self-luminous at the temperature of combustion the faint light shown by burning gases which do not give rise to solid or liquid particles, cannot be due to the glowing of the heated products of combustion....

"It may be urged that emission of light by hot gases is very faint and therefore easily overlooked when the temperature is not very high. The possibility of this must be admitted and it is very desirable that the experiments should be repeated at still higher temperatures and under more accurate conditions so as to determine the limiting temperature at which heated gases become undoubtedly self-luminous. The fact that gases do not emit light at a temperature of over 1500° C proves, however, that the luminosity of the flame is not due to the combustion products being self-luminous. The behavior of the flame also furnishes evidence of this. If we provide for a more rapid mixing of the gases to be burned, the flame becomes shorter, because the rate of combustion is increased, and hotter because less cold air is mixed with the burning gases. The flame also becomes shorter and hotter if the gases are preheated strongly before being ignited.

Since the ascending products of combustion must remain for an interval of time nearly at the temperature of the flame, we ought to get the opposite state of things in case the gases are self-luminous. The light of the flame ceases sharply at a very definite line which coincides evidently with the completion of the chemical action. This latter is therefore the cause of the light and not the heated products of combustion. If we assume that the gas molecules are each surrounded by a sheath of ether, an alteration of these sheaths of ether must take place when two or more such molecules combine. The resultant movement of the ether particles must be compensated by vibrations which may form the starting points for waves of light and heat. In a similar way one may account for the light-effects which are obtained when an electric current is passed through a gas. As I have shown a long time ago[1] when describing my ozone apparatus, all gases become conductors of electricity when we exceed what I have called the polarization maximum.... Since the current passing through the gas appears always to be accompanied by chemical action, one might account for the luminescence in the same way as with flames by assuming oscillatory transferences of the ether coatings round the gas molecules by means of which the transfer of electricity is accomplished. In that case the light of a flame could be called an electric light just as properly as the light of the ozone tube or of the Geissler tube.... The similarity in intensity and in color of the light from flames and from tubes through which an electric current passes is an argument for the cause of the light being the same in the two cases."

Mitscherlich[2] showed that no sodium line is obtained when sodium chloride or caustic soda is heated in a porcelain tube. This was confirmed by Pringsheim[3] for these and for other salts. On the other hand, the sodium lines were obtained when a suitable reducing agent was present. From

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[1] W. Siemens: Pogg. Ann., **102**, 66 (1857).

[2] Pogg. Ann., **116**, 504 (1862).

[3] Wied. Ann., **45**, 428 (1892); **49**, 347 (1893).

this Pringsheim concluded, very properly, that free metallic sodium was essential to the production of the D lines. He then prepared a cold flame by burning mixtures of carbon bisulphide and air. "The temperature of this flame can be made very low; the light is not brilliant but is distinctly blue and can readily be seen in a darkened room. The temperature is so low and the amount of heat generated is so small that one can hold one's finger in the flame indefinitely without feeling more than a moderate sensation of heat... The carbon bisulphide flame was regulated so that it just burned; the flame was very long and pointed in shape. Repeated measurements with a thermocouple, at the hottest portion of the flame just below the point, gave temperatures between 114° and 146° C. We can therefore say definitely that this flame continues burning at temperatures below 150° C, below the ignition temperature of the inflammable mixture which gives rise to the flame. The light emitted by this flame has a very considerable photographic action....The flame gives a continuous spectrum which is much weaker in the red part than in the blue and violet; it is very like the spectrum obtained when sulphur or hydrogen sulphide burns in the air. There can be no doubt but that we are dealing with gases which luminesce in consequence of chemical reactions and not in consequence of high temperature."

In the cold carbon bisulphide flame sodium chloride does not emit the D lines; but it does when the temperature is raised. From these and other experiments Pringsheim concludes that sodium salts give a yellow light in flames at lower temperatures than when the salts are heated in an indifferent atmosphere. From this postulate, it necessarily follows that in these cases sodium is set free by reduction and not as a result of thermal dissociation.

Pringsheim then heated metallic sodium in a porcelain tube and found that the vapor emitted the D lines. Since it is impossible to eliminate all traces of oxygen and since the porcelain tube itself consists of oxygen compounds, Pringsheim concludes that metallic sodium heated in neutral gases emits light only as a consequence of chemical processes and also that it is the reduction to sodium which emits light and not the oxidation of sodium.[1] Neither of these conclusions follows necessarily from the experiments and both have been attacked, as has also his other conclusion that "the assumption that gases can emit light by mere elevation of their temperature is a hypothesis demanded neither on experimental nor theoretical grounds."

An elaborate criticism of Pringsheim's views will be found in a series of papers by Paschen.[2] He admits, however, that the glowing of sodium vapor in the Bunsen flame is not merely a temperature emission.[3] "Paschen has compared the intensity of the two D lines in the sodium flame with the total intensity of a region completely enclosing the D lines, in the continuous spectrum of a black substance heated in the flame. The total intensity of the D radiation was more than twice as great as that of the region of the continuous spectrum which enclosed them, from which the inference can be drawn that something other than temperature is concerned with the emission of light by the sodium flame.[4] The same thing was found by Kayser and Paschen in the case of the ultraviolet bands of the arc, which were much brighter than a corresponding region of the spectrum of the positive crater, notwithstanding the fact that the temperature of the latter is higher than that of the arc proper."

Smithells[5] discusses the work of Hittorf, Siemens, and Pringsheim at some length.

"The experiments of Hittorf and Siemens may, I think, be held to establish two facts: (i) That air, carbon monoxide, steam, and carbon dioxide emit no sensible light when at an average temperature of 1500° C or perhaps 3000° C; (ii)

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[1] Cf. Fredenhagen: Drude's Ann., **20**, 141 (1906).

[2] Wied. Ann., **50**, 409 (1893); **51**, 1, 40; **52**, 228 (1894).

[3] Paschen: Ibid., **51**, 41 (1894); cf. Wood: "Physical Optics," 595 (1911).

[4] [Cf. however, Kayser: "Handbuch der Spectroscopie," **2**, 182 (1902).]

[5] Phil. Mag., [5] **37**, 248 (1894).

that the luminous part of flame is conterminous with the region of chemical action. They do not establish, I think, a third and most important conclusion, namely, that the luminosity is due directly to chemical action and not to heat. Before such a conclusion can be justified, we must be sure that the products of combustion in the flame do not exceed 1500° or 3000° C. It is assumed by Hittorf and Siemens, and has also been assumed by Pringsheim that we are justified in speaking of the temperature of a flame as the temperature indicated by thermometric instruments when they are introduced into the flame. This seems to me to be fundamentally erroneous. Such a recorded temperature is no doubt the effective temperature of the flame, but it is merely an average temperature.

"Every chemical student knows that the thinner the platinum wire he uses the hotter it becomes when introduced into a Bunsen flame, and it matters not whether the measurements of temperature depend on the fusibility of metals or salts, on specific heat, expansion, thermoelectric junctions, or electrical resistance, they are all open to the obvious objection that they only give the mean temperature of a considerable region of the flame uncorrected for conduction losses. What are we to say of the temperature of a candle-flame which will not melt a small bead of common salt but which will melt a platinum wire if pure and of a certain fineness?

"We may best deal with the matter by considering an ideal flame. Let us suppose that we have hydrogen issuing from a vertical cylindrical tube into oxygen gas, and let us consider a horizontal slice of the gas one molecule thick moving upwards in the tube.

"For the sake of simplicity we may neglect the molecular motion of the gas, and we will also suppose the gas to inflame spontaneously on meeting with the requisite oxygen. The slice of gas as it ascends the tube is retarded by friction at the edges and will issue with a conical form from the tube. Here it inflames and gives us a small conical flame. This flame would consist of a conical sheet of hydrogen, one molecule thick, combining with oxygen. If we are to measure the temperature at the locus of combination we must have a thermometric instrument small compared with the thickness of the sheet of combustion. If the instrument does not fulfil this condition, it will protrude into the unburnt gas within the cone and the cooling gases outside, and the temperature indicated will be the average of the whole region in which it is immersed.

"It may be objected that this is only an ideal flame, and that the conical sheath of flame actually obtained when hydrogen burns in oxygen has a very sensible thickness. This is no doubt true; but it must be at once pointed out that if the sheath of burning hydrogen has a sensible thickness, that is to say, if the hydrogen is burning on the outside surface, the inside surface, and in the intervening thickness of the sheath, hydrogen must all the while be passing through the sheath without undergoing combustion, in order that there may be some on the outer surface to maintain the combustion there taking place; and oxygen must be passing through from the outside to maintain the combustion of the hydrogen on the inner surface. If, then, we can get a thermometric instrument small enough to be wholly immersed in the region of combustion, the temperature indicated will not be that of the steam just formed but the average temperature of the hydrogen, oxygen, and steam within the sheath.

"From this I think it is plain that no thermometric instrument can possibly indicate the temperature of the product of combustion in a flame at the moment of formation. The temperature of 1500° ascribed to the hottest part of a Bunsen flame is therefore not the temperature of the products of combustion, and experiments that show these products to be non-luminous at a temperature even of 3000° C afford no proof that the luminosity of flame is due to some other cause than the mere high temperature of the products.

"How, then, are we to ascertain the temperature of the products of combustion? The only remaining method is to calculate it theoretically. This may be done if we make the assumption (which must be considered as doubtful in view of recent experiments) that the specific heat of gases does not alter greatly with increase of temperature.

"In the production of 18 grams of steam from 2 grams of hydrogen and 16 grams of oxygen there are evolved 57560 calories. The specific heat of steam being 0.4805 we have the rise of temperature:

$$t_2 - t_1 = \frac{57560}{18 \times 0.4805} = 6655°.$$

This temperature then (with the proviso as to the constancy of specific heat of steam) must be the temperature of the steam-molecules formed in a flame of hydrogen, assuming the whole heat liberated during the reaction to be stored in the newly formed molecules.[1] It is well known that steam begins to dissociate far below this temperature, but the question of dissociation only enters into our present consideration in this respect, that it forbids us to assume a hydrogen flame as consisting of molecules all in the act of combining. Whatever the degree of dissociation there is plainly some combination taking place, and if the heat liberated is stored in the molecules formed,[1] their temperature must rise to the theoretical 6600°. Even the average thermometric temperature of a hydrogen flame is above the temperature at which dissociation of steam begins, and there must be therefore a certain number of uncombined hydrogen and oxygen molecules in the flame. Our theoretical temperature of flame is no more an indication of its average temperature than its average temperature is a measure of the temperature of the steam which it contains. A gas may in fact exhibit a certain average temperature in two ways—it may have been raised to the average temperature by external heating or by internal chemical combination. In both cases the velocity of the molecules shows the same average, but this average is very differently compounded in the two cases. In the first case it

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[1] [This assumption of an adiabatic reaction requires justification.]

can be shown theoretically that the number of molecules having velocities four times the average is extremely small. In the second case (flames) we have a large number of molecules of intensely high temperature and a large number of low temperature. The average temperature is in this case compounded of two extremes, and there is every reason to anticipate a difference of physical qualities. This difference we might reasonably expect to manifest itself in the emission of light by the gas which contains the intensely heated molecules.

"Similar considerations apply to the temperature of carbonic acid produced in flames. The theoretical temperature for the combustion of carbonic oxide in oxygen is 7180° C.

"As neither steam nor carbon dioxide has been raised by external heating to anything approaching the temperatures we have indicated as accruing to them theoretically in the act of formation, it is still possible that the luminosity of flames in which they are produced may be due to high temperature in the ordinary sense of the term. The remark of Siemens that flames become smaller on increasing or heating the air-supply does not affect the conclusion arrived at, for it is not claimed that the luminosity of the products of combustion is of appreciable duration. Admixture with more air produces a smaller region of combustion, for it spares the combustible gas the necessity of wandering outwards to find the necessary oxygen. There would be in consequence a greater number of hydrogen and oxygen molecules uniting within a given space, the flame would be brighter but not necessarily larger, and this is certainly the case.

"It may be stated further, in relation to the luminosity of air, steam, and carbon dioxide, that having regard to their extremely small optical absorptive power it is not to be expected that they will show any great emissive power even when raised to very high temperatures. The degree of luminosity shown by a Bunsen gas-flame, assuming the products to have the temperature, calculated theoretically, appears to be just about what we might expect from *a priori* considerations."

Smithells subjects Pringsheim's views as to the luminescence of sodium vapor to a scathing criticism; but in the second part of the same paper he[1] modifies his attitude in regard to Pringsheim's views. "The experiments recorded in this paper afford some evidence as to the validity of the view of the origin of the flame spectra advocated by Pringsheim. If, as he concludes, the flame spectra commonly attributed to the alkali metals are a direct consequence of chemical processes occurring in the flame, the same is presumably true for the spectra of chemical compounds such as those of copper and gold. As a matter of fact, chemical changes do accompany the production of the spectra dealt with in this paper. Thus when cupric chloride is introduced into the flame, we have the formation of cuprous chloride and of cuprous oxide. The case of gold chloride is more important. In the case of this salt the spectrum is only developed when a large excess of chlorine or of hydrochloric acid and air is present; in their absence a considerable quantity of a spray or dust of the salt may be passed through the flame without giving any spectrum. The gold chloride, in fact, can only be maintained at a temperature sufficient to develop its spectrum when it is surrounded by an atmosphere either of chlorine or of an equivalent mixture of hydrochloric acid and oxygen. The gold chloride molecules, however, must not be regarded as remaining intact under these circumstances, for where a dissociable salt appears to be maintained in the undissociated state, through the presence of an excess of one of the products of dissociation, we ascribe it to the fact that, if momentarily dissociated, there is instantly a reunion. While, therefore, on the one hand, the high temperature at which the gold chloride spectrum is developed compels the separation of the gold and the chlorine, the large excess of chlorine, on the other hand, by the action of mass compels a recombination. Though

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[1] Smithells: Phil. Mag., [5] 39, 132 (1895).

this in a sense is tantamount to saying that the gold chloride molecules remain undissociated, the dynamical view of dissociation obliges us to picture a constant interchange between atoms of gold and atoms of chlorine. We are obliged to conclude, therefore, that the experiments recorded above are quite in harmony with the view advocated by Pringsheim.

"In a previous part of this paper I have offered some criticisms of the experiments on which Pringsheim bases his conclusion. Notwithstanding this I have never considered his view to be disproved: on the contrary, it seems *prima facie* to be a reasonable explanation of many phenomena occurring in flames. The facts I have now brought forward are in harmony with it, but I believe the evidence is still far from complete, and that further experiments are necessary to establish the doctrine that the light-emission from flames is a direct consequence of chemical processes."

Though it seems probable that heated sodium vapor is luminescent,[1] it is very difficult to eliminate all possibility of some chemical reaction taking place. This difficulty is not so serious with iodine vapor. Salet[2] heated to redness a large glass tube closed at one end. "The room was made dark and when the glass tube had cooled until it was just barely visible, a fragment of iodine was thrown into the tube which thereupon filled with luminous vapors. To obtain more brilliancy one heats the vapor of iodine in a Bohemian glass tube by means of an enameller's lamp. The contents of the tube look like a red-hot bar of iron. One may also volatilize iodine around a platinum spiral brought to a vivid incandescence; the luminous vapor rises like a real flame about the spiral. It is a case of *flame without combustion*. The light from the iodine gives a continuous spectrum, or rather a confused primary spectrum; one perceives traces of characteristic channellings but no lines of the secondary spectrum."

Smithells[3] has also experimented with heated iodine

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[1] Evershed: Phil. Mag., [5] 39, 471 (1894).

[2] Ann. Chim. Phys., [4] 28, 34 (1873).

[3] Phil. Mag., [5] 37, 252 (1894).

vapor. "At the suggestion of Sir G. G. Stokes, I tried the experiment of heating iodine vapor. This, being strongly absorptive at ordinary temperatures, might be expected to emit visible radiations at comparatively low temperatures. The experiment was made by filling the bowl of a 'churchwarden' tobacco-pipe with iodine and closing with a lute of plaster of Paris. The stem was laid along a Fletcher tube-furnace and strongly heated. The bowl of the pipe, which protruded about one inch from the other end, was shielded from stray light and viewed against a background of black velvet. When the stem was heated to such temperature as could be obtained with the unforced draught of air, the issuing stream of iodine vapor was not luminous, but when the furnace was fed with a blast of air and the temperature sufficient to soften the pipe, the iodine became luminous and the vapor presented the appearance of a pointed yellowish flame, about an inch in length. A similar appearance was obtained when a glazed porcelain tube was substituted for the pipe-stem so as to exclude all possibility of furnace gases diffusing into the interior. My attention was subsequently drawn to the fact that the effect had already been described by Salet[1] and had been achieved in a simpler way.

"The experiment may best be performed as follows:—a piece of hard glass tube about half inch diameter and five inches long and closed at one end is suspended horizontally by platinum wires from the ring of a retort-stand and heated along its whole length by the flame of a flat Bunsen burner. This should be done in the dark, and the burner removed as soon as the glass is seen to glow. The tube is allowed to cool till it has just ceased to glow, and then a long piece of platinum foil, bent into a trough and filled with iodine is passed into the tube and the iodine tipped out. The tube is immediately filled with the glowing vapor of iodine. This can be made to glow still more brightly by a reapplication of the flame. How much of the luminosity is due to the iodine and how much

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[1] Pogg. Ann., 147, 319 (1872).

to the hot glass may be seen at any moment by blowing out the iodine vapor by a puff of air. The effect is very marked, and there seems no room to doubt that the glowing is due to hot iodine vapor. The lowness of the temperature seems to forbid the suggestion that the glow may be due to combination of the iodine with oxygen or to the dissociation and recombination of the atoms of the iodine molecule.

"The result of this experiment is in conformity with the views already expressed as to the luminosity of flame, and enables us to see that, while colorless gases like those forming the products of the ordinary combustion are not likely to glow at the average temperature of a flame, they would at some higher temperature emit visible radiations."

Evershed[1] has confirmed and extended the experiments of Salet and of Smithells.

"To sum up, then, it appears that besides iodine, the vapors of bromine, chlorine, sulphur, selenium, and arsenic can all be made more or less incandescent by heating to the temperature at which the glass combustion tube softens, and the light emitted by each of these glowing vapors appears to give a perfectly continuous spectrum; while the corresponding absorption spectra are selective. Thus there is no such close relation between emission and absorption as is implied by Kirchhoff's law of radiating bodies. There seems, however, to be a general relation between the total absorbing and radiating power for the visible rays: those vapors which are highly colored and absorb strongly in the visible spectrum also radiate conspicuously in that part of the spectrum, while colorless, non-absorbing vapors, such as phosphorus, emit no perceptible light when heated.

"That the glowing in these cases differs in no way from the glowing of heated solids seems, to say the least, extremely probable, for there is no evidence whatever that chemical changes accompany the luminosity; and there is besides the fact that when direct combination does occur between the

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[1] Phil. Mag., [15] 39, 465 (1895).

vapor and the gas in which it is heated, as in the case of iodine in hydrogen, and possibly also arsenic in hydrogen, there is no luminous effect at all.

"It may be questioned, however, whether molecular dissociation may not be concerned in the radiation, or alternate dissociation and reaggregation of the atoms of the molecules. For, according to the kinetic theory, at a given temperature and pressure the vapors may contain a certain proportion of free atoms distributed among the more complex molecular groups, but the individuality of these uncombined atoms will continually change while the proportion remains the same, for there will be a constant reaction or interchange going on between the atoms and the molecules. The emission of light may be supposed to depend on this act of union or disunion of the atoms, the radiant energy being derived indirectly from the heat supplied to the system to maintain the temperature.

"Thus in the case of the diatomic gases iodine, bromine, and chlorine, a proportion of the molecules I_2, Br_2, Cl_2 may dissociate into 2 I, 2 Br, 2 Cl; and sulphur vapor may similarly dissociate from S_6 to $3S_2$, and so on. From recent determinations of the vapor densities of the halogens, it appears that iodine begins to dissociate between 600° and 700° C, at a pressure of one atmosphere.[1] Chlorine, on the other hand, remains at a normal density corresponding to Cl_2 between about 200° and 1200° C[2]. With regard to the former element, the temperature at which dissociation commences (say 600°) is not much above that at which the glowing is first seen, and as in most of the experiments the iodine or bromine vapor is largely diluted with a neutral gas, so that the partial pressure is a good deal less than one atmosphere, it might well be supposed that dissociation was going on even at the lowest temperature at which the glow can be seen. But in the case of chlorine, dissociation begins at some 500° above the temperature of my experiments (assumed at about

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[1] Crafts and Meier: Ber. chem. Ges. Berlin, 13, 851 (1880).

[2] Crafts: Ibid., 16, 457 (1883); also Jahn: Ibid., 15, 1238 (1882).

700°); moreover, there is no dilution of gas, which is observed at the atmospheric pressure, so there can be no question of dissociation here; or at any rate, as there is no independent evidence of it, we have no more right to assume it as a cause of luminosity than we have in the case of glowing solids.

"But, apart from the fact that chlorine can be made incandescent although it is not dissociating, it appears that the general relation mentioned above between radiation and absorption of the visible rays, and the fact that the intensity of the glowing of the more absorptive vapors (the others being too difficult to observe) appears to follow closely that of a solid raised simultaneously through the same range of temperature,[1] gives strong support to the view that there is no essential difference between gases and solids in the manner in which they radiate, at any rate under the conditions of the foregoing experiments. If dissociation were concerned, say, in the case of glowing iodine, one would expect the intensity of the light to increase rapidly when the temperature is made to approach the actual temperature of dissociation, where the maximum interaction of the atoms occurs. It should in fact increase in a much greater ratio than in the case of a glowing solid. But I have failed to detect any evidence of such relative increase on the part of either iodine or any glowing gas. Further, a decrease of density (by exhaustion or dilution) will facilitate the dissociation, and thus should tend to counteract the reduction of luminosity due to a smaller number of molecules concerned. But no such effect is in fact to be seen under these conditions."

Konen[2] comes to much the same conclusion. "The glow spectrum was obtained by means of a platinum spiral which

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[1] The radiation from iodine may easily be compared with that of a solid at the same temperature, by placing a small piece of carbon inside the heated portion of the glass tube previously described. Also when the glass contains opaque particles, these are seen to glow with the same intensity as the iodine, whatever the temperature, when the vapor is of sufficient density to give the maximum luminosity.

[2] Wied. Ann., **65**, 279 (1898).

was heated by the current inside a tube filled with iodine vapor. The luminescence of the iodine vapor begins at about 550° and is stronger the denser the vapor, thus corresponding to the absorption. Bands can only be detected at densities below about 1.4 (with reference to air), and are very hard to see because the intensity of the glow spectrum is then very low.

"If the temperature of the vapor is raised, the intensity of the glow spectrum first increases, then becomes constant, and begins to decrease perceptibly above 700°. With the closed apparatus previously described it was not possible to go much above 800°, since the packings then ceased to hold and the iodine diffused out extraordinarily rapidly. By means of the platinum spiral it is possible to obtain the glow spectrum at still higher temperatures. One then has to deal with the absorption of the cooler iodine vapor near the walls of the tube and possibly with reactions between platinum and iodine. Nevertheless, there is undoubtedly a decrease in emissivity with rising temperature. With the change in the intensity and in the appearance of the glow spectrum there is a completely parallel change in the absorption spectrum and the intensity decreases with rising temperature. I have not been able to make either the glow spectrum or the absorption spectrum disappear entirely.

"The glow spectrum is especially interesting because this is one of the few cases where one can obtain a visible spectrum merely by heating a gas. It has therefore been used by Ebert, Kayser, and Smithells as an argument against Pringsheim in the discussions over Pringsheim's paper on Kirchhoff's law. Ebert and then Pringsheim, however, raised the point that an explanation might be found in the dissociation of iodine which increases with rising temperature.[1]

"My experiments lead me to reject this explanation and to conclude that the glow spectrum is a true temperature

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[1] Since Pringsheim limited his conclusions explicitly to line spectra (Wied. Ann., 51, 441 (1894)), the glow spectrum has nothing to do with the case (cf. Paschen: Wied. Ann., 52, 228 (1894).

emission. Since the glow spectrum can be obtained over a continuous range of temperature, it cannot be due to a complete dissociation taking place at a definite temperature. If the glow is due to a continuous dissociation and recombination of the same number of molecules, its intensity must be proportional to the number of decompositions and will therefore reach a maximum when the vapor is half dissociated. The falling off of the emissivity begins, however, much below this limit and seems to indicate that the glow spectrum is furnished by the same undecomposed molecules which give the absorption spectrum. The glow spectrum decreases as they decrease."

While it seems to be fairly well established that such colored gases as iodine and sodium emit light when heated, Smithells and Dent[1] "found it impossible to render cyanogen incandescent at the highest temperature obtainable in a tube furnace."

Stark[2] considers that one may have an incandescence due to electrical or chemical causes, and that such an incandescence will not follow Kirchhoff's law. He believes that line spectra are due to collisions between positively charged atoms and negative electrons, univalent mercury ions giving the first line spectrum of mercury, and bivalent mercury ions the second line spectrum of mercury. Stark believes that a band spectrum is obtained when positively charged atoms unite with a negative electron. Thus there should be one band spectrum when bivalent mercury ions change to univalent mercury ions, and another spectrum when univalent mercury ions change to electrically neutral mercury atoms.

The question as to the luminescence of gases has been complicated unnecessarily by people having insisted entirely on a thermal luminescence, such as they say we have with solids, or entirely on chemiluminescence. In the case of solids we have

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[1] Jour. Chem. Soc., **65**, 609 (1894).

[2] Drude's Ann., **14**, 532; **16**, 511, 513 (1905).

chemiluminescence whenever we have phosphorescence. As we approach black body radiation for a solid or a liquid, we approach complete thermal luminescence. With gases we should expect to get thermal luminescence in all cases and chemiluminescence in some cases. If we have a practically colorless gas, we are very far from black body conditions and the thermal luminescence should be correspondingly small. "A substance that remained absolutely transparent at the highest temperatures would never glow."[1] Wood[2] says that "very few cases are known in which visible radiations can be obtained by merely heating a gas or vapor. An immense amount of work has been done by Pringsheim and others in endeavors to obtain a luminous emission from gases as a result of high temperature alone. Efforts in this direction have been, almost without exception, in vain, and Pringsheim came to the conclusion that, at least for temperatures which could be commanded in the laboratory, gases remained dark."

The two striking cases of luminescence on heating are iodine and sodium, both giving vapors with high absorption, which should give relatively high thermal luminosity. Less luminescence is obtained with chlorine, sulphur, selenium and arsenic,[3] substances which absorb less strongly in the visible spectrum than iodine or sodium, and more strongly than hydrogen, nitrogen, carbon dioxide, or water vapor. We should therefore expect to get a luminescence from hydrogen at any moderate temperature only when a chemical reaction of some sort is taking place, including ionization, of course. This is the conclusion reached by some of our prominent physicists.[4] "Hydrogen gas, under ordinary conditions, can be regarded as the most transparent substance known. Even the very short waves discovered by Schumann, which are powerfully absorbed by other gases, are freely transmitted by pure hydrogen. Hydrogen gas in the sun and stars shows

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[1] Kirchhoff: Pogg. Ann., 109, 293 (1860).

[2] "Physical Optics," 597 (1911).

[3] Evershed: Phil. Mag., [5] 39, 465 (1895).

[4] Wood: "Physical Optics," 433 (1911).

strong absorption lines, coincident with the emission lines seen when the gas is excited by electrical discharge in vacuum tubes. Many attempts have been made to determine the conditions necessary for the exhibition of absorption in the laboratory. Various observers have recorded seeing the red hydrogen line reversed in the spectrum of hydrogen tubes, but it is only within the last year or two that the exact conditions necessary for the exhibition of the phenomenon have been determined. The absorption only takes place while the gas is in a condition of luminescence, *i. e.*, while it is excited by the discharge. Pflüger[1] used as a source of light a capillary tube filled with hydrogen at low pressure, excited by powerful discharges from an induction coil with Leyden jars in the secondary circuit. The light from this tube was passed through a wider tube, also containing hydrogen at low pressure and placed in the same electrical circuit. By this arrangement the emission of light by the source was confined to the moments during which the gas in the wider tube was in a condition to absorb. The red line was seen distinctly reversed. Soon after, Ladenberg and Loria,[2] using a similar arrangement, reversed both the red and green lines, and obtained photographs showing the selective dispersion and magnetic rotation in the vicinity of the red line....

"This experiment shows that the passage of an electrical discharge through hydrogen gives rise to the formation of dispersion electrons, which are not present in the gas normally. Hydrogen, then, when ionized, or brought into a state of luminescence by the electrical discharge, has quite different optical properties from ordinary hydrogen. Sodium vapor possesses these properties normally, in the absence of any *electrical* stimulus, and *probably* in the absence of any excitation coming from without, though it is possible that an ionization necessary for selective absorption and dispersion results from the passage through the vapor of the light necessary

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[1] Drude's Ann., 24, 515 (1907).

[2] Verh. deutschen. phys. Ges., 10, 858 (1908).

for observing the phenomena. The dispersion does not, however, depend upon the intensity of the transmitted light, which shows that the effect is very small, if it exists at all."

While sodium must give some thermal luminescence, it does not follow at all that we may not be dealing in part with chemiluminescence. The preceding paragraph suggests this possibility. The following quotations show that Wood[1] goes quite a bit farther.

"The greater part of the evidence which we have obtained thus far regarding the structure of the atom indicates that the centres of vibration which emit the spectral lines are negatively charged corpuscles. The positive charges appear to be associated with the atom as a whole, and the assumption is often made that the positive electrification is of uniform distribution. The Zeeman effect shows us that the D lines of sodium are due to vibrators carrying negative charges, a fact which is true of all other lines which show the effect. That a negative charge is associated with the centers of vibration which emit the D lines is also shown by the direction (positive) of the magnetic rotation of the plane of polarization, for waves of very nearly the same frequency as that of the D lines. As is well known, most band spectra do not show the Zeeman effect at all, consequently we are unable to apply this test to the investigation of the nature of the charge associated with the centres of emission of the lines of which the bands are made up. Quite recently Dufour has observed the effect in some band spectra as we have seen. Some of the lines which make up the complicated channelled absorption spectrum of sodium vapor have been found by the author to have the power of rotating the plane of polarization when the light is passed through the magnetized vapor in the direction of the lines of force....

"It looks very much as if the different lines of the principal (Balmer) series and their accompanying channelled spectra may be considered as produced by different entities. The

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[1] "Physical Optics," 537, 579 (1911).

enormous increase in vapor density necessary to bring out the higher members of the series may perhaps be ascribed to the possible circumstance that the entities producing them are present in smaller numbers. It appears to me that there are two hypotheses which we may make: First, that the Balmer lines and their accompanying spectra are caused by atoms which have lost one, two, three, four, etc., electrons. Secondly, that they are produced by aggregates or complexes of one, two, three or more atoms. In either case it seems probable that the members would be present in continuously increasing numbers."

If sodium vapor, when heated, breaks up into smaller aggregates or loses electrons we have chemical reactions in the broader sense of the word which may or may not give rise to light, since we know that all reactions emit light when the reaction velocity is sufficiently high.[1] The problem is, then, to distinguish the chemiluminescence from the thermal luminescence. If the intensity of the light emitted is greater than the intensity of black body radiation for the same wave-lengths at the same temperature, we must be dealing with chemiluminescence. The converse is not true,[2] though it is apparently considered true by many physicists who consider that they have established the existence of a purely thermal luminescence when they show that the intensity of light emitted by a fairly transparent body is not greater than the intensity of black body radiation. As soon as the error of this reasoning is seen, it is also clear that quantitative measurements of intensity of light are only occasionally of value for this problem until there is a better agreement as to what the intensity of the thermal luminescence of a fairly transparent substance should be at any given temperature.[3]

For the present, the most satisfactory line of attack seems to be to guess at the reactions taking place in any given

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[1] Bancroft: Jour. Franklin Inst., 175, 129 (1913).

[2] Kayser: "Handbuch der Spectroscopie," 2, 182 (1902).

[3] Ibid., 2, 38 (1902); Wood: "Physical Optics," 594 (1911).

case and then to determine to what extent these reactions account for the light actually emitted.[1] Whatever light cannot thus be accounted for can be called thermal luminescence for the time being. If one is going to proceed along these lines, care must be taken to distinguish between the light actually emitted by the system and the light which reaches the eye, because the light may have been modified by passing through a colored medium in the flame, the arc, or the vacuum tube. Mitscherlich[2] calls attention to this source of error. "If an excess of a substance be added so that the vapor be not heated sufficiently, and if the substance be one which gives a spectrum containing only a few lines, so that an absorption spectrum is readily obtained, one gets the absorption spectrum because the brilliant light from the centre of the flame passes through the surrounding vapor of the substance. One gets this phenomenon when sodium burns or when one volatilizes a great deal of sodium in a hydrogen flame. The easiest way to study it is to add varying amounts of iodine to a hydrogen flame. If only a little iodine is added, one sees the new spectrum which I discovered; with an excess of iodine in the flame, the absorption spectrum is obtained. The centre of the flame is white hot and this light passes through the iodine vapors which absorb a portion of it just as is the case if one looks through iodine vapor at a candle flame."

Wood[3] calls attention to the effect due to absorption in the case of hydrogen and to the effect due to suspended particles of sodium. "An observation recorded by the author several years ago enables us to show the absorbing power for hydrogen gas for light of a wave-length corresponding to that of the red line without the aid of any special apparatus. A vacuum tube is arranged for end-on observation having a bore of about 3 mm. The pressure of the hydrogen should be 6 or 7 mm and it should be excited by a large induction coil with a spark

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[1] Cf. Kayser: "Handbuch der Spectroscopie," **2**, 159 (1902).

[2] Pogg. Ann., **121**, 487 (1864); cf. Wüllner: Ibid., **120**, 164 (1863): Wied. Ann., **8**, 599 (1879).

[3] "Physical Optics," 446, 639 (1911).

gap in the circuit. It will be noticed that the color of the discharge, seen through the side of the tube, is rose-red, but a bluish white when viewed end-on. This is due to the fact that the long column of glowing gas exercises a powerful absorption for the light of the red line, and little or no absorption for the other rays. That the dependence of color upon the direction in which the observation is made is not a result of the difference of total intensity can be shown by viewing the end-on discharge through a pair of Nicol prisms by which the intensity can be reduced until it is equal to that of the discharge, seen through the side of the tube....

"Allusion has been made to the deep violet light scattered by a condensing cloud of sodium vapor. The author has frequently observed that the color of the light transmitted through the sodium tubes, in the experiments upon the optical properties of the vapor, was colored a deep yellow instead of blue, as is usually the case. It was difficult to understand this at first, since the vapor is perfectly transparent to blue light, and somewhat less so to yellow-green light. The cause was finally found to be a scattering of the violet and blue rays by the fog of condensing vapor, which was so powerful that none of these rays was transmitted. The phenomenon was investigated further with the large tube used in the experiments on fluorescence, some potassium being introduced into the retort. The light from the arc was focussed about 20 cm in front of the retort and the tube powerfully and rapidly heated by a blast lamp. Under this condition the vapor is puffed out in clouds from the aperture of the retort, and the condensing clouds are most wonderfully colored, red and orange predominating. It was found that if the heating was carefully regulated, a steady state could be maintained in which the fog scattered red light at the outer boundary, where the cone of rays entered it, yellow a little further in, and green at the point where it was first forming and where the cone of rays passed out into the vapor in which it was of course invisible. The cone of rays seen from the side, which can be accomplished by looking in at the edge of the glass window, resembled a spectrum, the blue end of which was wanting. A potassium fog thus scattered longer waves than a sodium fog, and the scattering power is confined to a comparatively narrow region of the spectrum, which apparently varies with the size of the particles in the fog. It is probable that we are dealing with something analogous to the granular deposits of these metals already described."

A few words are perhaps necessary in regard to the assumption, made by Smithells,[1] that the temperature of the hydrogen flame is about 6655° and that of the carbon monoxide flame about 7180°. The temperature, calculated from the heat reaction and from the specific heats, can be reached only in case there is no conduction of heat away from the reacting system and in case there is no dissociation. To speak of percentage dissociation in case of a single molecule seems to mean nothing at all; on the other hand it is quite certain that the temperature of a single molecule cannot rise to that at which complete dissociation takes place no matter what the heat of reaction is. All calculations like that of Smithells are therefore of doubtful accuracy.[2] There is a more serious objection to the calculation. Even if we admitted that portions of the flame reached 6000°–7000°, these portions cannot heat an added substance to any such temperature.[3] Therefore we cannot postulate any 6000° for sodium chloride added to the flame; and yet there seems to be no fundamental difference between the behavior of sodium chloride and that of other luminous gases. It seems also as though too much stress has always been laid upon the apparent contradiction that a candle flame will melt platinum and will not melt sodium chloride. Either the candle flame will melt a bead of sodium chloride having the same diameter as the thin piece of platinum, or the platinum wire acts as a catalytic agent and raises the temperature of the flame at that point. This latter sug-

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[1] Phil. Mag., [5] 37, 250 (1894).

[2] Liveing and Dewar only claim 3000° for exploding gases. Phil. Mag., [5] 18, 172 (1884).

[3] Cf. Liveing and Dewar: Proc. Roy. Soc., 44, 244 (1888).

gestion has been made by Baikoff; but Haber claims that the facts do not warrant this.[1]

In the preceding paper[2] we have shown that metallic salts are dissociated more or less in the Bunsen flame or the oxyhydrogen flame, so that the free metals are present in the flame. Light may be emitted by the reactions setting free the metal or oxidizing it or both. We have made a qualitative experimental study of the behavior of tin salts and of copper salts in the flames, and we hope that this will show the value of the method. Eventually, quantitative meaurements will have to be made; but this cannot be done satisfactorily until we know the reactions which are taking place.

Speaking of the spectrum produced by tin salts, Salet[3] says:

"When a very little stannous chloride is volatilized in a current of hydrogen and the latter ignited, the flame is colored blue. Fumes of stannic oxide are formed which make the edge of the flame white. The core of this flame is composed of two concentric cylinders, the inner one of which is blue and the outer one faintly colored carmine. One can analyze these different colored lights separately without modifying their state. It is sufficient to focus the image of the flame on the slit of the spectroscope."

Salet gives a photograph of the spectrum obtained and has measured some of the characteristic lines. He says: "The inner cylinder gives a continuous spectrum (with a maximum in the blue); the red cylinder gives a single line at 610 and a diffuse band at 618. The position of the line coincides with the lithium β. The outer, blue portion of the flame gives a band spectrum.

"If the flame is cooled by introducing a cold object, there is obtained near the cold body a beautiful red colora-

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[1] Haber: "Thermodynamik technischer Gasreaktionen," 279 (1905). Cf. Kayser: "Handbuch der Spectroscopie," 2, 161 (1902).

[2] Bancroft and Weiser: 18, 213 (1914).

[3] Ann. Chim. Phys., [4] 28, 5 (1873).

tion.... When the bromide is used instead of the chloride, or when a drop of bromine is placed in the chloride flame, the inner cylinder previously colored blue becomes a clear green without the [outer portion of the] flame itself ceasing to be blue and to give the spectrum previously described. The green cone gives a continuous spectrum.

"In the cooled flame the green color appears in immediate contact with the cold body and with a brightness that might be mistaken for phosphorus if the spectrum were not examined. Near the green layer and in the less cold region, the red color appears, giving the bright line at 610. The iodide of tin gives similar results. The innermost cone is yellow and its spectrum is continuous as with the chloride and bromide.

"The results of these experiments show that the different volatile compounds of tin introduced into the flame of hydrogen each give three spectra, two of which are common to all. The first spectrum is obtained in a reducing atmosphere when the temperature is only moderately high. This is perhaps the primary spectrum of tin and is characterized by the small band at 610. The second spectrum is obtained at the highest temperature and in the zone of combustion. It is due to the oxide of tin and is characterized by the band spectrum rich in lines. The third spectrum is obtained in the innermost region where the temperature is low. It is a continuous spectrum and varies with the salts employed, being blue with the chloride, green with the bromide and yellow with the iodide."

In order to check up the work of Salet and to make any additional observations, the following experiments were performed:

Tin Salts in the Hydrogen Flame

Stannous Chloride.—A piece of hard glass tubing a half inch in diameter and a foot long was drawn out to a jet which was turned up at a right angle to the tube. The end was tipped with platinum so as to prevent contamination of the flame by the materials of which the glass was composed. A little porcelain boat containing anhydrous stannous chloride was placed in the tube; hydrogen was run in and lighted at the jet. The boat containing the salt was heated gently, and the salt was vaporized and carried into the flame. The small innermost cone is colored blue and is surrounded by a bright red cylinder. Outside of this is a cone of a light green color, strikingly similar to the light green coloration obtained so frequently in the succeeding experiments on direct union. The upper portion of the flame is blue in color. When there is not too much of the salt present the color is more of a reddish blue, due to the carmine color that diffuses up through the flame. If the amount of chloride becomes still less, the flame is colored only slightly and the carmine predominates. If, at this point, the flame is cooled by allowing it to impinge on a cold porcelain tube, the feeble carmine becomes a beautiful bright red in the region of contact. This may be shown even more strikingly by holding the cold tube vertically in the inner reddish region of the flame. The carmine brightens up and is seen as a separate and distinct flame unmarred by any blue-green coloration. The red luminescence obtained in this way is far more striking then one would suppose from Salet's account, being even more brilliant than the red flame of lithium. The lower portion of this flame has a reddish yellow appearance and the edge is more of a yellowish white, due to the excess of salt and to the stannic oxide formed.

The flame was examined with the spectroscope and was seen to be composed of bright bands, the clearest and sharpest of which are in the blue-green portion.

Stannous Bromide.—If the bromide of tin is fed into the hydrogen flame just as the chloride was, the innermost cone is distinctly more of a blue-green than in the case of the chloride. This blue-green portion is surrounded by the red cylinder and this in turn by the light green, as was seen with the chloride. The upper portion of the flame is blue, but it has slightly more of a greenish tinge than was observed with the chloride. When the flame containing just a little of the salt is cooled, the red is seen strikingly, just as in the preceding case. When examined with the spectroscope, the flame appeared very similar to that of the chloride. The same bright bands in the blue and green were present.

Stannous Iodide.—Using the iodide, the innermost cone is greenish yellow. There is considerable green in this flame but the upper part is bluish and shows the same spectrum as given with the chloride and bromide. By cooling the flame containing only a little of the salt, the red luminescence is obtained brightly as in the previous cases.

If there is too much of the salt present in any of the above cases when the flame is cooled, the red luminescence is marred by blue-green luminescence or yellowish green, as the case may be, similar to that obtained in the relatively cold, innermost portion of the flame. The cause of the differing colors with different salts in the colder portion of the flame will be discussed later.

Tin Salts in the Bunsen Flame

When the salts are introduced into the Bunsen flame by means of a platinum wire, results similar to those in the hydrogen flame are obtained. The flame of the bromide is more markedly bluish green throughout, while that of the iodide is distinctly more yellowish throughout than in the hydrogen flame. The carmine color is obtained in all three cases. The chief difference in the two flames is that the various colors are more strikingly separated in the hydrogen flame than they are in the Bunsen.

Luminescence by Chemical Action

In an attempt to duplicate these more or less separate and distinct colors chemically, the following experiments were tried:

Tin and Oxygen or Air.—A small piece of tin was heated with a blast lamp, and a jet of oxygen made to impinge on it. The metal burned with an incandescent bright flame. The flame was so brilliant that it was impossible to distinguish any particular color.

Tin and Sodium Peroxide.—A small quantity of tin was placed in a porcelain crucible and melted. The surface of oxide was scraped off, exposing the bright metallic surface. On this was dropped a small quantity of sodium peroxide. There was a flash at first, after which one could see the tin burning with a bright, light green luminescence. The green light emitted by this reaction is seen more clearly by sprinkling just a few grains of the peroxide on the fresh surface. The sparks formed show a distinctly green coloration.

Tin and Chlorine.—The metal was placed in a little boat in a combustion tube and heated. Chlorine from a cylinder was passed through a wash-bottle and then over the molten metal. The latter glowed all over with a greenish yellow glow and finally burst into flame, burning up brightly. Near the surface of the tin the color of the flame was a sort of violet-blue, but the tip of the flame was a decided green. The reaction resulted in the formation of stannic chloride.

Stannous Chloride and Chlorine.—To show that the light green luminescence in the above case was due to the oxidation of stannous to stannic chloride, a few grams of the dehydrated stannous chloride were placed in a piece of combustion tubing and chlorine passed over them. The oxidation took place without heating. If the chlorine was run very slowly, light green sparks flashed up as the little particles of the salt oxidized. If the salt was matted and the chlorine passed over it, the whole surface oxidized with a light green luminescence. If the chlorine was run in quite fast, the flame flared up; but the color of the luminescence was marred by a yellowish color due partly to the excess of salt picked up by the rapid stream of chlorine and partly to the yellow color which chlorine itself will impart to a flame when it is run into it. This yellow color may be seen by impinging a slow stream of chlorine on the very edge of a Bunsen flame.

Tin and Bromine.—Bromine was boiled in a flask and the vapors were conducted over the heated tin as described above. The tin burned with a flame that appeared reddish as viewed through the bromine vapor. A light green luminescence could frequently be seen extending up through the flame, but it can be seen more clearly if the metal is heated very hot indeed. When this is done, little fragments of the metal spurt up and burn with a distinctly green luminescence.

Tin and Iodine.—A piece of hard-glass combustion tubing was closed at one end and then bent at a right angle. The fused end was filled with iodine. Tin was placed in the horizontal portion and was heated about six centimeters from the iodine. This heating was sufficient to vaporize some of the iodine which attacked the tin, the latter burning with a flame. The flame appeared reddish yellow in color as viewed through the dense fumes, but unmistakable green flashes were often seen. Even after burning for several minutes to ensure the removal of all oxygen, the green flashes were still visible.

Tin and iodine were made to combine in still another way. About five grams of pure tin were melted in a porcelain crucible. While in a molten condition, the film of oxide was scraped off exposing the fresh surface, and on this were dropped some small pieces of iodine. This reacted vigorously with the tin and a little green light could be seen through the reddish yellow vapors. If these vapors were blown away by a gentle current of nitrogen, it was clearly seen that the light green luminescence was emitted at the reacting surface and was the result of the union of tin with iodine to form stannic iodide.

Stannic Oxide and Oxygen.—When stannous oxide was heated in a current of oxygen, it burned to stannic oxide. If the oxygen were allowed to run in fast, so that very rapid oxidation took place, the stannic oxide became heated to incandescence and the color of the luminescence was obscured. If, on the other hand, the stannous oxide were heated more gently and the stream of oxygen cut down so that the reaction proceeded more slowly, the light due to incandescence was not so marked and flashes of a distinctly light green color could be seen creeping along the tube. It is evident that this greenish luminescence is the characteristic color emitted by the oxidation of stannous to stannic oxide.

Hydrogen Flame impinging on Metallic Tin.—A piece of chemically pure sheet tin was placed on a piece of iron and a small hydrogen flame was made to impinge upon it. In a short time a thin layer of the metal was heated almost to the melting point and then the flame was moved slowly back and forth over the heated area. In the flame at the very surface of the tin could be seen the characteristic bright red luminescence that was noted so strikingly when volatile tin salts were placed in the flame. This red light was seen only in the distinctly reducing atmosphere near the surface of the metal. Above it, in a more oxidizing region, the red gave place to the light bluish green luminescence. Particles of tin flew up into the flame and became incandescent, but this did not prevent the two separate and distinct colors being seen clearly. At the surface of the sheet tin, where the atmosphere was reducing and where metal was in excess, the reaction from metal to stannous tin was practically the only one taking place. In the region above this the oxidation from stannous to stannic tin was complete.

Experiments on Reduction.—When some tin salt, such as the chloride, is placed in the Bunsen or hydrogen flame, there is a partial dissociation of the salt into its elements.[1] This may be shown experimentally by introducing a cold object into the hottest portion of the flame into which the tin salt has been placed. A mirror of metallic tin may readily be precipitated. The metal that is set free by dissociation is continually recombining, and the previous experiments show that the reactions involved in this combustion emit light. Salet observed the presence of stannic oxide in the periphery of the hydrogen flame when a tin salt was introduced into the flame. The oxide is clearly seen as a white or yellowish white envelope around the flame. That the brownish stannous oxide is present as an intermediate product in the complete oxidation may be verified by precipitating a film on a cold tube held well within the flame.

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[1] Bancroft and Weiser: Jour. Phys. Chem., **18**, 213 (1914).

It was thought that perhaps the reverse reaction, of reduction or dissociation, might emit a characteristic light, and the following reactions were tried: Anhydrous stannous chloride and aluminum were ground together and heated. Reduction took place rapidly. The rate of the reaction was varied from almost an explosion to just a slight flash by varying the relative amounts of the constituents, but no characteristic luminescence was obtained. Anhydrous stannic chloride was ground finely and mixed with an equivalent amount of finely ground calcium carbide.[1] In order to prevent the carbon set free in the reaction from burning and giving a colored flame, the mixture was placed in a porcelain boat in a tube and nitrogen passed over it. On heating this mixture, reduction took place rapidly and metallic tin was formed. There was, however, no characteristic luminescence.

From these results and from analogy with Smithells' experiments on copper, which will be given later; it seems that the reactions of reduction or dissociation are not the important ones in causing the luminescence when tin salts are introduced into the flame. The data at hand may be summarized thus:

1. The carmine color is produced in the flame with all the different volatile compounds of tin and with the metal itself. It is obtained most strikingly as a distinct bright red cylinder in the reducing portion of the hydrogen flame and is particularly marked when the flame is cooled.

2. The carmine color is obtained at the surface of a sheet of metallic tin when the latter is burned by impinging a hydrogen flame against it.

3. The light green to blue color is obtained in the hot oxidizing region surrounding the region in which carmine is the characteristic luminescence. Viewing the flame with an ordinary spectroscope, the light is found to be made up chiefly of bands, the brightest of which are in the green and blue-green portion.

4. When tin is burned by impinging a hydrogen flame

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[1] von Kügelgen: Zeit. Elektrochemie, 7, 541 (1901).

against it, a light green luminescence is obtained in the strongly oxidizing region above the cooler reducing region where the carmine luminescence predominates.

5. The halides give a color in the innermost region of the flame that is fundamentally blue-green in color but is modified considerably by the specific salt employed.

6. Tin + Oxygen (sodium peroxide) = Light green.
7. Tin + Chlorine = Bluish violet to green.
8. Stannous chloride + Chlorine = Light green.
9. Tin + Bromine = Green.
10. Tin + Iodine = Light green (yellowish?).
11. Stannous Oxide + Oxygen = Light green.

12. Tin salts introduced into the flame are dissociated to a greater or lesser extent into the elements.

13. The direct reactions of oxidation, rather than the reverse ones of reduction or dissociation, are responsible for the characteristic luminescence.

With these data the following explanation of the reactions producing a part at least of the different colors in the "tin" flame is suggested as most probable:

It is evident that the reactions emitting the light in any specific flame are going on all the time and that it is the sum of these light effects that the eye sees. For example, two reactions A and B are responsible for the light emitted in a certain flame, reaction A alone giving a red light and reaction B alone giving a green light. If the conditions in a certain region of the flame are such that reaction A is more energetic than reaction B we should expect the effects of B to be hidden to a greater or lesser extent by the predominating effect of A. In accord with this assumption, the resulting color at this point would be chiefly red. If, on the other hand, reaction B is the predominating one, the small amount of red is hidden and in this region we get a green coloration chiefly. When neither reaction A nor B predominates, a luminescence is obtained that is a combination of the two light effects. The presence of any colored substance in the flame will of course have its effect in modifying the specific color of the light due to the reaction.

The following reactions are going on in the "tin" flame and from the data offer a most probable explanation of a large portion of the luminescence obtained:

1. Reaction of metallic tin to stannous ion (or stannous salts) = Carmine luminescence.

2. Reaction of stannous ion to stannic ion (or stannic salts) = Light green luminescence.

Since metallic tin gives a characteristic arc spectrum in hydrogen, it seems better to assign the carmine luminescence temporarily to the reaction $Sn \longrightarrow Sn^{\cdot\cdot}$ and the light green luminescence to the reaction $Sn^{\cdot\cdot} \longrightarrow Sn^{\cdot\cdot\cdot\cdot}$. In a later paper we hope to be able to show what part, if any, of the luminescence is due to the reaction from stannous ion or stannic ion to undissociated salt.

The Carmine Luminescence

The carmine light is obtained in all "tin" flames but is most striking in the region that is but slightly oxidizing. It may be secured almost entirely unmarred by the bluish green luminescence characteristic in the strongly oxidizing zone. By cooling the flame, the carmine luminescence is markedly increased. Since stannic oxide is the stable form at the highest temperature of the flame, it would be expected that the combustion of the metal would be complete and that the green luminescence in the hot oxidizing zone would predominate over the red. On the other hand, in the cooler, less strongly oxidizing region we should expect stannous oxide to be formed momentarily in considerable amounts and the light emitted by the intermediate reaction from metal to stannous tin to predominate. It may be shown, as a matter of fact, that stannous oxide is formed in the region of the flame where red predominates, by precipitating a film on a cold tube. A further proof that the red luminescence is produced by the reaction from metal to stannous tin is obtained when tin is burned by impinging a hydrogen flame on sheet tin. At the surface where tin is in excess and where the flame is but slightly oxidizing and relatively cool, tin burns to stannous tin with the red luminescence, while in the most strongly oxidizing region, just above the surface, the blue-green luminescence appears.

All the above facts are in direct accord with the assumption that the reaction from the metal to stannous tin gives the red or carmine luminescence, while the further oxidation to stannic tin gives the light green coloration.

The Light Green Luminescence

When tin was made to combine slowly with oxygen or with the halogens the characteristic color was a light green and the final product was a stannic salt. Furthermore, when stannous oxide was burned to stannic oxide, either directly or by impinging a hydrogen flame against tin, a light green luminescence was observed. A similar color was obtained when stannous chloride was oxidized to stannic chloride by passing a slow current of chlorine over the anhydrous salt. This is in accord with the assumption that a light green luminescence is emitted when stannous tin reacts to form stannic tin. It is evident from the data on direct union that, when a stannic salt is formed, the color emitted by the reaction from metal to stannous tin is masked by the predominating green.

Since we know that stannic oxide is formed in large amounts in the flame we should expect the flame to emit considerable green luminescence. As a matter of fact a light green cylinder surrounds the carmine cylinder in the hydrogen flame. The spectroscope shows bright bands in the green and the blue-green portion. When there is considerable salt in the flame, the upper portion, particularly, appears to the eye blue rather than light green. This may be due to one of two things: either there is another reaction which we have not identified and which gives a luminescence with a maximum in the blue, or what is more probable, in view of our present experimental evidence, the presence of substances in the flame may modify the color of light emitted by the fundamental reaction. The great importance of this latter factor on the color of the light we see, when certain salts are introduced into the flame, seems to have been overlooked to a large extent. That it is an important factor and one that cannot be neglected, may be shown by the following experiments and observations:

When the chloride of tin is introduced into the Bunsen flame by means of a platinum wire, the predominating color is blue throughout, while it is green throughout with the bromide. Attention has already been called to the thermal dissociation that takes place when tin halides are brought into the flame. The free halogen being colored to a greater or lesser extent we should expect it to modify the color of the light emitted by the fundamental reactions taking place in the flame. That this is true may be readily shown experimentally. Into a glass cell about three inches square and one-half inch thick, a small amount of liquid bromine was placed. This vaporized and partly filled the cell with bromine fumes. The cell was then set close to and on a level with a Bunsen flame colored blue with stannous chloride. Looking at the flame through the thin layer of bromine vapor, the blue gives place to a decided green. This is exactly in accord with what we should expect. Another example is seen in the case of the iodide of tin. When this salt is introduced into the Bunsen flame, the flame is colored yellowish with some green. When iodine vapor acts on metallic tin the flame is reddish yellow with occasional flashes of green. If, however, a crystal of iodine is dropped on a piece of melted tin and the excess of iodine vapors blown away, so that the light emitted by the direct action of tin with iodine may be closely observed, it is found not to be yellowish but distinctly greenish. The yellow color of the iodide itself is doubtless the most important factor in masking the green luminescence.

These experiments serve to show the unquestioned influence of colored material in the flame on the color of light emitted. The difference between the so-called "chloride," "bromide," and "iodide" spectra, while not wholly, are at least partially due to this effect. The effect of the presence of halogen may be threefold.

1. The specific color of the free halogen, independent of anything else.

2. The screening effect of the colored substance which would modify the color of light emitted by the fundamental reactions.

3. The reactions of the heated halogen itself. Thus the reaction from ion to molecule of halogen or the reaction of halogen with the constituents of the flame. We have marked experimental evidence of such an effect in the case of heated iodine vapor.

This brings us naturally to a discussion of the specific colors obtained in the relatively cool inner portion of the flame when the tin halides are introduced into it. With the chloride this is blue, with the bromide green, and with the iodide yellow. From the above experiments these are exactly the differences in the three flames which we should predict. The salts are dissociated in part at a relatively low temperature and the free halogen unquestionably has an effect. This is most marked at the lower temperature of the inner cone or in direct contact with the cold tube when there is considerable of the salt present in the flame. The color of the undissociated salt will also have an effect that will naturally be most marked in the coolest portion of the flame where dissociation is not complete.

In the blue portion of the "tin" flames the chief effect of colored substances other than the halides will be brought about by the vapors of tin oxides and especially of metallic tin itself, since the latter is present in considerable quantity. Lockyer and Roberts[1] have shown that tin vapors have a distinct absorption in the blue and this would account for the luminescence, where tin vapor is present, being rather more blue than light green, as the reactions on direct union would

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[1] Proc. Roy. Soc., 23, 344 (1875).

indicate. Further evidence of this may be shown by holding the cooled porcelain tube vertically in the blue portion of the flame when not too much salt is present. A film of tin oxide, tin, and non-dissociated salt forms slowly and the whole flame takes on more of a light green than of a blue appearance.

So far we have considered the luminescence of the relatively cooler inner cone, only to show how the fundamental light green or blue-green luminescence was modified by the presence of a specific halogen or salt. We have not yet considered the reaction producing the blue-green luminescence. This must evidently be due tc the reaction from stannous to stannic tin. In order to account for this reaction we have to postulate that the stannous salt (volatilized into the flame directly or formed by reduction of stannic salt) does not dissociate entirely in this region, but under the existing conditions reacts partly to form tin and stannic salt. If this assumption be true, then the reaction to stannic salt in this region ought to be prevented by the addition of a suitable reducing agent, and no blue-green luminescence whatsoever should be obtained. This is exactly what was found to be the case when a very little formaldehyde vapor was introduced along with the hydrogen. The experiment was carried out as follows: The two parallel arms of a Y-tube were attached to two pieces of combustion tubing each about $^5/_8$ inch in diameter and 8 inches long. The other arm was bent at a right angle, drawn out to a jet, and tipped with platinum. A small porcelain boat containing some stannous chloride was placed in one of the pieces of combustion tubing and a few drops of water were placed in the other. Hydrogen from a cylinder was conducted through both pieces of combustion tubing and lighted at the jet. A pinch-cock was placed on the piece of rubber tubing which conducted the hydrogen into the tube containing the water. The flame was changed neither in size nor shape by opening and closing this pinch-cock. With the pinch-cock closed, the flame was colored by volatilizing some of the stannous chloride. On opening and closing the pinch-cock the appearance and structure of the colored flame remained unchanged. The water was then boiled and the vapor carried into the flame along with the stannous chloride. All of these blank tests showed no change whatsoever in the character of the original flame. Finally, the water was replaced by two or three drops of a solution of formaldehyde. This was heated very gently and the pinch-cock alternately opened and closed. The blue-green luminescence in the inner cone disappeared completely when the pinch-cock was opened and reappeared when it was closed. A minute amount of formaldehyde was sufficient to prevent the oxidation and the accompanying luminescence.

Conclusion.—The above experiments show that certain reactions are going on in the tin flame and that these reactions are accompanied by a characteristic luminescence. No claim is made that the reactions from metal to stannous ion and the further oxidation to stannic ion are the only ones that emit light, but it has been proven that these are fundamental. The reactions from the ions to the undissociated salts unquestionably have some effect, as has been intimated in the above discussion. We hope to show the extent of this effect by subsequent investigation on electro- and cathodo-luminescence.

Experiments with Copper Salts

When copper halides are placed in the flame, results are obtained similar to those when tin halides are employed. If the chloride is introduced into the Bunsen flame by means of a platinum wire there is seen to be a yellowish light in the immediate vicinity of the bead. Outside this is seen a blue coloration and beyond this on the outside of the flame an intense grass green. If the bead becomes too hot there extends up through the flame a diffuse reddish brown color, most marked at the very edge of the flame. If the bromide is used instead of the chloride, the colors are similar but the inner portion is just a little more greenish blue than the light blue of the chloride. With the iodide this inner portion is distinctly more greenish blue.

When the halogens are introduced into the hydrogen flame in a manner similar to the halides of tin, the flame appears almost entirely grass green except when a very large excess of the salt is used. When this is the case, a little light blue can be seen; but the outer portion is always green. Gouy[1] has called attention to the fact that, by holding a cooled body in the green flame to which copper chloride has been added, blue is obtained in the cooled region.

When salts other than the halides are used, the flame appears almost entirely green, the lines and bands being less pronounced in the blue and violet. The spectrum of salts other than halides were most satisfactorily obtained by the use of a Gouy apparatus greatly simplified and modified so that it could be attached directly to a Bunsen burner. It was found, as Gouy describes, that the sulphate and nitrate of copper give the same spectrum. The dilute solution of chloride gives a spectrum containing the same lines and bands as the sulphate and nitrate. With a more concentrated solution of chloride a different spectrum is obtained. This is in no way out of harmony with the theory that the luminescence in the flames is a result of chemical action. As shown in the case of tin flames, the presence of certain specific material in the flame modifies the appearance of the light emitted by the fundamental reactions. This explains in part the fact that a flame containing just a little cupric chloride gives the same spectrum as that of sulphates and nitrates while a different spectrum is obtained with a greater concentration of chloride. Indeed Lecoq de Boisbaudran[2] has shown that by varying the amount of cupric chloride introduced into the flame, one can get almost anything from a spectrum exactly like that produced by copper nitrate, sulphate, or oxide, to the other extreme, when the amount of chloride is so great that a continuous spectrum is about all that is obtained. Smithells[3] speaks of one spectrum of the series being the "nor-

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[1] Comptes rendus, **85**, 439 (1877).
[2] "Spectres lumineux," 157.
[3] Phil. Mag., [5] **39**, 125 (1895).

mal" spectrum of cupric chloride. It is difficult to see how any one spectrum of the series can be the "normal" one any more than another, since each is dependent on the specific conditions obtained in the flame. The spectrum observed in the case of chloride is materially affected by the absorptive and screening effect of the cupric chloride. Furthermore, the introduction of an excess of salt cuts down the temperature and the constant dissociation and oxidation taking place, and affects the reactions and correspondingly influences the luminescence. This at once calls to our attention the relative ease of dissociation of the halides as compared with sulphates, nitrates or oxides. All of these factors and another that will be considered later naturally cause the specific differences observed with the different copper salts.

Gouy[1] has further shown that with a strongly reducing flame the nitrate, acetate, and oxide of copper show well-defined red bands in the interior portion of the flame. Under the right conditions this red coloration predominates over the usual grass green.

The following experiments show that certain fundamental reactions are going on in all "copper" flames and that these are accompanied by characteristic luminescences.

In a previous paper[2] attention has been called to the fact that copper salts, particularly the halides, dissociate very markedly in the flames and that it is possible to precipitate copper on a cold tube, especially from the hottest portions. By precipitating films from various parts of the flame it may be shown that the liberated metal oxidizes, forming again the specific salts in the cooled or cooler portion of the flame or forming the oxides of copper. If a film is precipitated from the intense green outer portion, it is found to be quite dark, which looks as though cupric oxide existed chiefly in the green part of the flame. This was quite unexpected. Debray and Joannis[3] have shown that solid cupric oxide breaks down

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[1] Comptes rendus, **84**, 231; **85**, 439 (1877).

[2] Bancroft and Weiser: Jour. Phys. Chem., **18**, 213 (1914).

[3] Comptes rendus, **99**, 583 (1884).

readily into cuprous oxide and oxygen when heated. Smithells[1] states that the oxygen tension within and around the ordinary flame is far too small for cupric oxide to exist in appreciable amounts. Conditions seem to be different, however, with the vaporized oxide. We have never succeeded in precipitating anything approaching a pure cuprous oxide from any flame. Since we can precipitate cuprous chloride, or such metals as zinc, it is not probable that the trouble is due to an oxidation of cuprous oxide to cupric oxide at the moment of precipitation. We conclude, therefore, that cupric oxide, like stannic oxide, is the oxide chiefly present under flame conditions. This conclusion is confirmed by the behavior of the flame. Experiments were made as in the case of tin to find out whether the reactions involved in the dissociation or reduction of copper salts were important factors in the luminescence observed. Negative results were obtained as with tin. This was the conclusion reached by Smithells.[2] He found, by means of the flame separator, that the inner portion had no green but only a lurid luminosity, whereas the outer cone gave the usual spectrum. The reverse reaction of reduction or dissociation took place in the inner cone without any luminescence, while oxidation in the outer cone produced luminescence. This leads us to conclude that the reactions of major importance are those of oxidation.

Copper Vapor in the Gas Flame.—When copper vapor is introduced into the hot gas flame by volatilizing some of the metal in a furnace, it burns in the flame unquestionably chiefly to cupric oxide. Since we shall show by special experiments that the change from cuprous salt to cupric salt emits blue light, the intense grass green luminescence must be due to the change from copper to cuprous salt.

Copper Powder in the Gas or Hydrogen Flame.—If very finely divided copper powder is sprinkled into the flame, it likewise burns with the same grass green coloration.

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[1] Phil. Mag., [5] 39, 128 (1895).
[2] Proc. Chem. Soc., 8, 8 (1892).

Copper and Oxygen.—Attempts to burn massive copper in oxygen gave negative results due to the rapid formation of a film of oxide at the surface or to the particles heating to incandescence, masking the characteristic light. The method finally used was to drop very finely divided metallic copper on fused potassium nitrate. In this experiment the ordinary commercial copper powder cannot be used because the stearine, coating the small particles, burns with a reddish flame. Very finely divided cupric oxide was reduced with hydrogen and this subjected to long grinding in an agate mortar to get the particles as finely divided as possible. Potassium nitrate was heated till oxygen began to come off and then minute amounts of the copper powder were sprinkled on the surface. Larger particles burned with incandescence masking the characteristic light; but a green luminescence could frequently be seen with the smaller particles. Occasionally sparks were obtained that appeared light blue rather than greenish. This experiment is decided proof that the oxidation of copper under suitable conditions is accompanied by a luminescence.

Cuprous Oxide and Oxygen.—Since the difficulty of burning copper in oxygen is so great, it was thought possible to burn cuprous to cupric oxide. This was carried out as follows:

A small amount of pure cuprous oxide was placed in a piece of combustion tubing about two feet long and one-half inch in diameter. One end of this tube was connected to a cylinder of oxygen and the other was left open. The oxide was heated very gently and the oxygen was turned on occasionally until the temperature was such that the oxide would just burn. When such a temperature was reached the oxygen was turned on very fast indeed. This picked up the oxide and carried it the length of the tube. The cuprous oxide burned to cupric oxide, and a light blue luminescence was observed. If care was taken to have the temperature just right, and if the gust of oxygen was sufficiently strong, the light blue luminescence was quite bright, was continuous for a moment, and extended the full length of the tube. By this method of procedure myriads of fine particles of cuprous oxide were burned to cupric oxide, each with a little light blue luminescence. When the oxide was placed in a heap and then heated, while the oxygen was slowly passed over it, the combustion took place without any characteristically colored light.

Copper and Chlorine.—Attempts to burn copper by heating it and then passing a stream of chlorine over it always resulted in a cherry-red glow. It was thought possible to bring about the union of copper and chlorine by heating a large quantity of the copper very hot indeed and then impinging a stream of chlorine on the surface. To do this a large piece of copper was placed in a crucible in a furnace and heated until the melt bubbled and vaporized slightly. A little stream of chlorine was impinged on this and immediately copious fumes formed which had a dark reddish brown color. This color was obviously not due to the chemical reaction but rather to the color of the cupric chloride vapors formed in the presence of excess of chlorine above the molten copper.

Copper in Carbon Monoxide Flame.—When an excess of cupric chloride is placed in the carbon monoxide flame it is colored blue with a little green fringe. Smithells[1] found, by impinging a jet of hydrogen on a carbon monoxide flame colored blue with excess of cupric chloride, that a green color was obtained at the point of contact. The purpose of this experiment was to prove if possible that water was necessary for the formation of the green luminescence. This is not necessarily true, for if copper powder is sprinkled into a carbon monoxide flame it burns with a green luminescence, just as in the hydrogen or coal gas flame. Furthermore, it will be shown later that green is the predominating color on the outside of a chlorine flame burning in hydrogen.

Copper in the Flame of Hydrogen burning in Chlorine.—In this experiment the hydrogen was burned in a compartment through which chlorine was kept running in a constant stream.

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[1] Phil. Mag., [5] 39, 128 (1895).

When metallic copper or any copper salt was introduced into this flame it was colored blue and was surrounded by a brown-red coloration similar to that obtained in the gas flame when an excess of cupric chloride is added. Fredenhagen[1] states that if a jet of hydrogen be brought into this brown-red edge, the color becomes blue. What Fredenhagen actually did was to bring another hydrogen flame burning in chlorine alongside the first. With hydrogen burning in chlorine there is very little green and the predominating color is blue, because there is practically no formation of metallic copper in the flame and consequently no reaction from copper to cuprous salt. A film precipitated from this flame contained both cuprous and cupric chloride but no copper.

Copper or a Copper Salt in the Flame of Chlorine burning in Hydrogen.—In order to burn chlorine in an excess of hydrogen the following method was employed: Chlorine was run into the inner tube of a small blast lamp and hydrogen surrounded it. This was ignited and the flame was then thrust into a very large inverted test-tube. Soon all the oxygen was burned out of the test-tube and the only flame remaining was the chlorine burning in the surrounding atmosphere of hydrogen. The hydrogen was run in quite rapidly for several minutes, so that all traces of oxygen would be washed out and was lighted at the mouth of the test-tube. A piece of pure copper wire or a platinum wire containing some copper chloride was thrust up into the flame. The predominating color with hydrogen in excess was green. Of course, if the wire was thrust into the chlorine, blue was obtained at this point, just as we should expect from the previous experiment, but the edge, and particularly the tip, was grass green. A film could be precipitated from this flame that contained a little copper, but the chief product was cuprous chloride. By holding the wire on the very edge of the flame, but very little blue was obtained even though large amounts of copper chloride were present, as could be told by the unusually intense

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[1] Drude's Ann., 20, 152 (1906).

coloration of the hydrogen flame at the mouth of the test-tube. Near the end of the test-tube where the hydrogen starts to burn, air is burning in an excess of hydrogen. At this point there is a disc about an eighth of an inch thick colored entirely green, in marked contrast to the intense blue fringed with green in the flame of hydrogen burning in air.

Cathode Rays on Cuprous Iodide.—Under the influence of cathode rays cuprous iodide gives a purplish red luminescence.[1] Since cuprous iodide is the only one that exists, the reaction emitting this light is that from cuprous ion to cuprous salt.

The data secured may be summarized as follows:

1. Copper chloride introduced into the Bunsen flame by a platinum wire gives light blue fringed with grass green. There is a diffuse red coloration through the flame and especially at the tip. The bromide and iodide of copper give a similar coloration except that there is a tendency toward greenish blue in the inner portion.

2. Cooling a flame colored green by cupric chloride gives a blue in the cooled region.

3. A flame colored with an excess of copper chloride gives a spectrum that differs from that obtained with the nitrate, sulphate, or oxide. A part of this difference is due to the colored vapors of the chloride itself.

4. Copper salts dissociate in the flame and the subsequent oxidation is most important in producing the luminescence.

5. Cupric oxide is stable under the conditions of the Bunsen flame.

6. Copper vapors impart to a gas flame or a hydrogen flame an intense grass green color.

7. Copper powder sprinkled into the gas flame, the hydrogen flame, or the carbon monoxide flame, colors it an intense grass green.

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[1] Goldstein: Jour. Phys. Chem., 13, 54 (1909).

8. Copper + Oxygen (KNO_3) = Green chiefly and sometimes blue.

9. Cuprous Oxide + Oxygen = Light blue.

10. Copper + Chlorine. Burns with a red glow. When chlorine is impinged on molten copper, the cupric chloride vapors above it are violet-red in color.

11. An excess of copper chloride in a carbon monoxide flame colors it blue. A jet of hydrogen impinged on it gives green at the point of contact.

12. Copper in the hydrogen flame burning in chlorine gives chiefly blue with an edge of reddish brown.

13. Copper in the chlorine flame burning in excess of hydrogen gives chiefly green.

14. Copper chloride in air burning in hydrogen gives green.

15. There is a ruddy color in the interior of the copper flame, particularly marked when the flame is made strongly reducing.

16. Cathode rays on cuprous iodide give a reddish luminescence.

From the data at hand the following reactions that are going on in every "copper" flame suggest themselves as most important in producing the characteristic luminescence:

I. Copper ⟶ Cuprous ion = Green
II. Cuprous ion ⟶ Cuprous salt = Red
III. Cuprous ion ⟶ Cupric ion or Cupric salt = Blue

The Green Luminescence

When copper vapor or copper powder is introduced into a hot flame, the latter is colored intensely green, the extent of the green coloration being greater the higher the temperature. Likewise, when any copper salt is introduced into the flame the predominating color is green except in the region cooled by some means or another. Since the reaction proceeds chiefly to cupric oxide, it follows that the green luminescence of the stage from copper to cuprous oxide is more intense than, and masks the blue luminescence of, the stage from cuprous to cupric oxide. As a matter of fact, the spectroscope shows the presence of the blue luminescence in the green flame. This accounts for the fact that the flame colored with copper chloride is almost entirely green unless it is made relatively cool by an excess of the vapors. If the apparently green flame is cooled, dissociation to copper is diminished and consequently the reaction to cupric ion should become relatively more predominant at the point of cooling and blue should be the characteristic color. As a matter of fact this is exactly what Gouy found to be the case. Since we know that cuprous oxide burns to cupric oxide with a blue luminescence, exactly the same thing should be obtained with a flame containing no chlorine.

When copper or a copper salt is placed in the chlorine flame burning in hydrogen we should expect the reaction to cuprous ion to take place chiefly. Under these conditions green should predominate. Experiment shows this to be the case. If a copper salt or copper itself is introduced into air burning in hydrogen, the reducing atmosphere would tend to emphasize the reaction from metal to cuprous ion and not to cupric ion. The color of the light under such circumstances is green. This was seen even in the presence of a very large excess of copper chloride.

If a jet of hydrogen is impinged on a flame colored blue by an excess of a copper halide, for example, the carbon monoxide flame, the effect would be to retard locally the action to cupric ion and cause the reaction to cuprous ion to predominate. This should result in the formation of green light at the point where the hydrogen impinged. Green actually does predominate at this point.

All of the above facts show that whatever the salt introduced into the flame, a green luminescence occurs if the conditions are such that the reaction from copper to cuprous ion should and does predominate.

The Ruddy Luminescence

Gouy found that a red luminescence is seen at a point near the base of the flame containing oxide, nitrate, or acetate of copper if the flame is made strongly reducing.

This is different from the brownish red on the edge of the hydrogen flame burning in chlorine when copper is introduced into it. It is known that cathode rays on cuprous iodide give a red luminescence and this is unquestionably due to the reaction from cuprous ion to cuprous salt. It is only reasonable to suppose that a similar reaction could be brought about in the flame to a sufficient extent to cause the red color to predominate. Gouy secured these conditions with a very strongly reducing flame.

The red diffuse color that is found on the edge of the hydrogen flame burning in chlorine and the Bunsen flame fed with a large excess of copper chloride is largely due to the color of the cupric chloride vapor which is violet-red and to suspended particles of the solid cupric chloride, which is reddish brown.

The Blue Luminescence

The direct combustion from cuprous to cupric oxide gives a light blue luminescence strikingly similar to the blue of the Bunsen flame. As above stated, Gouy has found that cooling the green flame causes blue to appear at the point of cooling. At the temperature of the flame the reaction from copper to cupric salt is the chief one, but if the flame is cooled locally we should expect what little cuprous salt was present to oxidize completely, and consequently the flame should become more blue at that point. When copper is put into the hydrogen flame burning in chlorine the excess of chlorine naturally results in the complete oxidation. The result is a blue coloration in striking contrast to the flame produced if chlorine is burned in excess of hydrogen.

When doing the experiments, it was noticed that the blue obtained when the halogens are present is relatively more intense than when no halogen is present. On the other hand, the blue luminescence is obtained in all flames and may be secured markedly by the direct oxidation of cuprous to cupric oxide. By impinging the vapors of oxygen or of the halogens on an intense green copper flame, the extent of this difference may be shown in still another way than before given. The halogens produce a marked blue to greenish blue at point of contact, depending on the halogen employed, whereas the fainter blue luminescence due to the oxidation of cuprous to cupric oxide is largely masked by the intense green. If chlorine is mixed with air in a concentration of two or three percent by volume, no more blue is obtained than with pure oxygen. The cause of this difference has been explained to be due in part to the specific color of the halogens and to the vapors of the salts themselves. It is unquestionably true that the reaction to the non-dissociated salt also has an influence in determining the specific nature of the blue luminescence. There is no reason at all why the reaction with the formation of cupric oxide should be the same quantitatively as the reaction with the formation of cupric chloride.

This specific difference, however, is of minor importance at present compared with the fact that the same general reaction produces qualitatively the same luminescence.

The general conclusions of this paper are:

1. An absolutely transparent gas will emit no light at any temperature unless some reaction takes place.

2. A colored vapor may emit a purely thermal luminescence; but that is notp roof that the actual luminescence in any given case is entirely a thermal luminescence.

3. It is not necessarily a proof of thermal luminescence to show that the luminescence of a moderately transparent vapor has a lower intensity than the corresponding luminescence of a black body at the same temperature.

4. There seems to be no justification for the assumptions that temperatures of about 6600° are reached in the hydrogen flame and of about 7200° in the carbon monoxide.

5. It is distinctly misleading to say that a candle flame will melt platinum and will not melt sodium chloride.

6. Since the luminescence of any given flame may be due wholly or in part to chemiluminescence, it is important to

determine what reactions are taking place in the flame and to what extent the luminescence is due to these reactions.

7. When studying flame reactions, it is necessary to distinguish carefully between colors due to emission and to absorption. This source of error has not always been taken into account in the past.

8. A qualitative study has been made of the flame reactions of tin and the salts of tin.

9. The reaction of tin to stannous salt gives a carmine luminescence; and of stannous salt to stannic salt a green luminescence, the latter being the more intense as a rule. It is probable that the carmine luminescence is due chiefly to the reaction $\mathrm{Sn} \longrightarrow \mathrm{Sn}^{\cdot\cdot}$ and the green luminescence chiefly to the reaction $\mathrm{Sn} \longrightarrow \mathrm{Sn}^{\cdot\cdot\cdot\cdot}$; but no experiments have yet been made to show what luminescence, if any, is due to the reaction of stannous or stannic ion to the corresponding undissociated salt.

10. No characteristic luminescence has yet been detected for the reverse reactions.

11. The differences between the spectra of tin chloride, bromide, and iodide are due to the absorption spectra of the halogens and the salts; also to the light emitted by the reactions of the halogens themselves.

12. A qualitative study has been made of the flame reactions of copper and the salts of copper.

13. The reaction of copper to cuprous ion gives a green luminescence; from cuprous ion to cuprous salt a red luminescence; from cuprousion to cupric salt a blue luminescence. It is probable that the blue luminescence is due chiefly to the reaction $\mathrm{Cu}^{\cdot} \longrightarrow \mathrm{Cu}^{\cdot\cdot}$; but no experiments have yet been made to show what luminescence, if any, is due to the reaction of cupric ion to cupric salt.

14. The intensity of the green luminescence is so great that the unaided eye does not notice any blue in the ordinary copper flame even though the copper burns chiefly to cupric salt.

15. No characteristic luminescence has yet been detected for the reverse reactions.

16. The violet-red color of undissociated cupric chloride vapor must not be mistaken for a luminescence.

17. It has proved possible to account satisfactorily in a qualitative way for all the phenomena in connection with tin flames and copper flames.

Cornell University

ADSORPTION BY FILTER PAPER

BY M. A. GORDON

In a paper on capillary analysis, Bayley[1] says: "Sometime ago, while holding a wet patch, formed by dropping a solution of silver nitrate upon filter paper, in a stream of hydrogen mixed with arseniuretted hydrogen, I noticed that the metal was contained in the centre of the blot, and that the edges for about half a centimeter inwards were entirely free from metal. After being exposed to the gas, the blot presented the appearance of a black spot surrounded by a broad ring of water.... Drops of other metallic solutions were placed upon filter paper and submitted to the action of sulphuretted hydrogen. I found that in some cases the metal extends to the edge of the spot and even seems concentrated there, while in others a water-ring surrounds the patch of sulphide. Further inquiry demonstrated that solutions of the same metal present the first or second of these phenomena, according as they are concentrated or dilute. Taking a strong solution of copper sulphate and diluting portions of it, I found that at one degree of solution the metal spreads outwards just as far as the water, and that with solutions more dilute than this, the water is separated from the metal, which remains in the centre. The more dilute the solution, the broader is the external water-ring. The exact strength of solution to give the former appearance varies with the temperature, and with the kind of paper used; the metal in a warm solution is more mobile than if the solution were cold.

"The blot formed by a drop is larger on the whole, but the mobility of the metal is increased in a greater proportion than that of the water. A close Swedish paper is more efficacious in separating the salt than a loose-textured piece of common filter paper.

"A great difference is found to exist among the salts

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[1] Jour. Chem. Soc., 33, 304 (1878).

of various metals; the salts of silver, lead, and the persalts of mercury, when moderately concentrated, give a wide water-ring, while the salts of copper, nickel, and cobalt must be much more dilute to present the same appearance. Cadmium seems especially able to pass through filter paper.

"A solution of copper sulphate containing 0.001 gram of copper per cc was found to give a water-ring; at the same temperature and with the same piece of Swedish paper, a solution of cadmium sulphate of less than half that strength gave a blot in which the cadmium extended perfectly to the edge. Metals appear to act in this respect as though other metals were absent; this property of cadmium, therefore, affords an elegant means of detecting it in the presence of metals, the sulphides of which are black. The considerably dilute solution is dropped upon filter paper, and the blot allowed to extend as far as possible (this should be done in all cases) and the sulphuretted hydrogen then turned on. The black patch is found to be surrounded by a vivid yellow ring of cadmium sulphide.

"A solution rich in nickel, cobalt, or iron may in like manner be examined for these metals, in presence of smaller quantities of copper, lead, mercury, and silver. The blot spreads, is exposed to sulphuretted hydrogen, and afterwards held over a bottle of ammonium sulphide, when the water-ring becomes black. This method, however, is extremely suited to the detection of cadmium. It was found that the presence of free acid much increases the mobility of copper, so that before testing for cadmium in this manner, the solution, if acid, should be made slightly alkaline by ammonia."

It seemed desirable to find out something about the conditions under which cadmium could be detected in the presence of copper by means of this diffusion method. Instead of following Bayley's work exactly, experiments were made with strips of filter paper dipping into small volumes of the solution. A rather heavy, white, blotting paper was used and was cut into strips 2.5 cm wide. The first set of experiments was made to show the relative rates of diffusion of equimolecular solutions of cadmium sulphate and of copper sulphate. A known volume of the solution was allowed to diffuse up the strip for a certain length of time. The height to which the solute rose was determined by placing the strip in a bottle containing a little ammonium sulphide. The data are given in Table I and are shown graphically in Fig. 1.

TABLE I

Volume of solution, 1 cc; time, 30 minutes

Molar conc.	Rise in filter paper, cm			
	Cadmium sulphate		Copper sulphate	
	H_2O	Cd	H_2O	Cu
0.025	9.1	6.0	8.6	5.3
—	9.2	5.9	9.2	5.5
0.05	9.2	7.4	9.0	6.6
—	9.2	7.4	8.7	6.5
0.1	9.2	8.6	9.0	7.7
—	9.5	8.7	9.0	7.6
0.3	9.2	9.2	9.0	8.6
—	9.1	9.1	8.7	8.5
0.4	9.0	9.0	9.1	9.1
—	9.0	9.0	9.1	9.1
0.5	9.1	9.1	9.2	9.2

It will be seen from these data that cadmium sulphate diffuses farther than copper sulphate, except of course for concentrations at which copper sulphate gives no water-ring under the conditions of the experiment. At concentrations of 0.3 molar and higher the cadmium sulphate moves as fast as the water and copper sulphate does the same at concentrations of 0.4 molar and higher. At lower concentrations the cadmium sulphate diffuses distinctly faster than the copper sulphate and should therefore be detected in the outer ring in case the difference in rate is not diminished in a mixed solution. Bayley's concentration of one milligram of copper per cubic centimeter or one gram per liter corresponds to a little less than 0.02 molar. On the other hand, these experiments show that if the relative rates remain the same, one could not detect cadmium in case the molar concentration of the copper sulphate was approximately double that of the cadmium sulphate or at higher concentrations than about 0.4 molar. Bayley's own experiments show that the relative rates of diffusion in mixed solutions are not necessarily the same[1] as the ratio of the rates of the substances taken separately, because he found that "the presence of free acid much increases the mobility of copper."

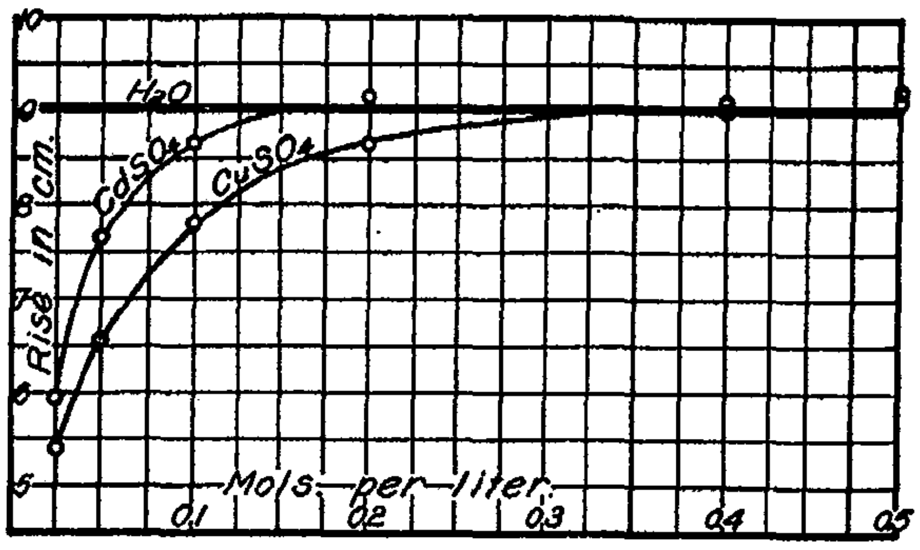

Fig. 1

Relative Diffusion of $CuSO_4$ and $CdSO_4$
Volume of Solution = 1 cc
Time of Diffusion = 30 minutes

As it was no part of the plan to make an exhaustive study of these phenomena, the next set of experiments was made with the more concentrated solution prepared by mixing equal volumes of 1 molar copper sulphate and 1 molar cadmium sulphate. Apart from contraction or expansion the resulting solution was half-molar with respect to each salt and might reasonably have been expected not to show any

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[1] Cf. also Freundlich: Kapillarchemie, 164 (1909).

separation of the salts. A strip of blotting paper was allowed to stand with one end in the solution until the liquid had risen to a height of 6 or 7 cm. It was then placed in a bottle containing ammonium sulphide. The strip was colored a dark brown by the copper sulphide as far up as the liquid had diffused. The yellow of the cadmium sulphide could not be seen. If the strip was now allowed to stand in the liquid again or in water until the liquid had diffused 0.2 to 0.4 cm farther and was then placed in the bottle again, the yellow cadmium sulphide became visible over the stretch through which the solution had just diffused. This presented some theoretical difficulties. If the salts had been precipitated completely by the ammonium sulphide there should have been a water-ring formed. If they had not been precipitated completely, why should there be only cadmium sulphide in the newly wetted zone? The most plausible explanation is that we are dealing with a case of fractional precipitation and solution. It is known that copper sulphide is precipitated before cadmium sulphide. In these experiments only the salts in the outer layer of the filter paper are precipitated. When this has taken place, the solution on the inside diffuses out and comes in contact with the mixed sulphides, and we have the reaction

$$CuSO_4 + CdS = CuS + CdSO_4.$$

If enough copper has been precipitated, the cadmium sulphate will diffuse alone and will be precipitated separately on treatment with hydrogen sulphide.

It seems quite likely that the diffusion method for the detection of cadmium in presence of copper may be used when the copper salt is not present in too great excess. Let us consider the different possibilities. We may have a solution of such a concentration that both the copper and the cadmium sulphate diffuse as fast as the water. This is the case that has just been described and it is possible to apply the method of fractional precipitation. It would also be possible to dilute the solution until a water-ring was formed on diffusion.

If the cadmium were present in sufficient relative amounts, it would show up without fractional precipitation. If we had a solution, however, so high in copper and so low in cadmium that the copper diffused as fast as the water while the cadmium did not, there would be, by hypothesis, no cadmium to be carried on as a result of fractional precipitation. Diluting the solution would not help matters because the cadmium would practically never go as far as the copper. On the other hand the solution could be concentrated by evaporation until the cadmium diffused as fast as the water and then the method of fractional precipitation could be applied. It is not likely that this test will be of much value in qualitative analysis because a negative result is not conclusive as to the absence of cadmium.

It is, perhaps, desirable to say a few words about the general theory of the formation of a water-ring in filter paper because there are several points in Bayley's work for which he offered no explanation and the text-books on colloid chemistry apparently make no reference either to Bayley or to Lloyd.[1] Ostwald[2] mentions the work of Schönbein (which was apparently unknown to Bayley and to Lloyd) and says that the phenomenon is evidently one of adsorption, which is perfectly true as far as it goes but does not give much in the way of detail. Bayley also saw that it was a case of adsorption though he could not make any especial use of this.[3]

"I therefore made a few experiments, in order to determine whether filter paper has any power of withdrawing silver salts from solution. 7.8703 grams of silver nitrate having been dissolved in water and diluted to 500 cc, a quantity of this solution was placed in a beaker, and a roll of filter paper sufficient to absorb nearly the whole plunged into it. After some minutes the filter paper was removed and as much of the liquid as possible squeezed into the beaker.

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[1] Chem. News, 51, 51 (1885).

[2] Lehrbuch allgem. Chem., 2nd Ed., 1, 1098 (1891).

[3] Bayley: Jour. Chem. Soc., 33, 304 (1878).

It is clear that the effect of this treatment, unless the paper possesses a power of retaining the salt, would merely be to slightly concentrate the solution by evaporation. Four experiments were made in this manner, fresh rolls of paper and fresh portions of the standard solution being used in each instance. Twenty-five cc of the solution, after treatment with the paper, were mixed with hydrochloric acid, and the precipitated silver chloride dried, ignited, and weighed.

"The results were as follows:

Solution used Cc	Ag found gram	Ag originally present gram
25	0.2182	0.2500
25	0.2306	0.2500
25	0.2353	0.2500
50	0.4760	0.5000

This shows that, after a roll of paper has been soaked for a few minutes in a solution of silver nitrate, the quantity of silver has materially diminished. A few experiments made by my friend, Mr. Weston, show that the same is true in the case of mercury salts."

Like other substances filter paper shows a selective adsorption for dissolved substances, taking up some very completely and others but slightly. If a few drops of different salt solutions be placed upon a piece of filter paper, the substance which is adsorbed the most will diffuse the least distance. In other words, we should expect the widest water-ring with the solution containing the most readily adsorbed salt.[1] With the same salt we should get the widest water-ring with the dilute solutions, which is exactly what Bayley found and what is shown by the experiments in Table I.

Bayley obtained wide water-rings with salts of silver, lead, and mercury in moderately concentrated solutions. He himself showed that silver nitrate is adsorbed by filter paper. Yorke[2] found "on filtering a solution of oxide of lead

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[1] Cf. Freundlich: Kapillarchemie, 156 (1909).

[2] Mem. Chem. Soc., 2, 399 (1845).

in lime water through a triple filter, that, whereas the original solution gave a deep black when tested by sulphuretted hydrogen, the filtered liquid gave but a pale brown; and it required that the unfiltered liquid should be diluted with thirty times its volume of water to produce the same test as the filtered. I then tried the effect of mere immersion of the paper in the aqueous solutions before used. A bit of filtering paper ten inches by two inches was boiled in distilled water and then put into an ounce phial filled with the aqueous solution; after remaining six hours the liquid was poured off and tested: it gave a pale brown, and it required that the liquid which had not been in contact with the paper should be diluted with ten times its volume of water to produce the same tint."

Schwalbe[1] says that lead salts are kept back quantitatively by cotton fibers and that one must not filter solutions of lead through paper in quantitative work. If the filter paper is washed with boiling water, the lead salt is fixed the more firmly. Skraup[2] found that lead acetate was decomposed by filter paper, the acetic acid being less adsorbed than the lead. Vignon[3] has shown that cotton wool adsorbs mercury salts so much that it decomposes mercuric chloride into free hydrochloric acid and basic salt or oxide. In the case of these metals we thus have confirmatory evidence of the obvious relation between degree of adsorption and extent of water-ring.

Herzog[4] gives some data on the adsorption of copper sulphate by cotton wool; but we cannot compare these data with those of Bayley on silver nitrate because Bayley does not give the weight of the filter paper added. It seems quite certain, however, that the silver salt is adsorbed more than the copper salt. Müller[5] has shown that filter paper possesses the property of taking up not inconsiderable quantities of

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[1] Die Chemie der Cellulose, 80 (1911).

[2] Sitzungsber. Akad. Wiss. Wien, 118, IIb, 564 (1909).

[3] Comptes rendus, 116, 517, 584, 645 (1893).

[4] Zeit. Farbenindustrie, 7, 281 (1908).

[5] Jour. prakt. Chem., 83, 384 (1861).

barium hydroxide from an aqueous solution of this substance and that such a solution should not be filtered through paper in quantitative determinations. In line with this are Schönbein's and Skraup's experiments[1] showing that barium hydroxide solutions give a wide water-ring.

Since adsorption is accompanied by evolution of heat, there will be less adsorption at higher temperatures and consequently the water-ring will be relatively narrower. This is what Bayley found, for he says that "the metal in a warm solution is more mobile than if the solution were cold." According to Skraup's measurements, sulphuric acid does not rise as high in filter paper as copper sulphate of equivalent concentration, and is, therefore, adsorbed to somewhat greater extent. If this is so, copper sulphate will be adsorbed relatively less from a mixture of sulphuric acid and copper sulphate; the metal will, therefore, give a narrower water-ring in an acid solution than a neutral one and this is what Bayley found. There is another way of looking at this which does not depend on the adsorption of sulphuric acid. If we assume that cellulose has a distinct adsorbing power for cupric hydroxide or for a basic copper salt, the adsorption will be less the more acid the solution and consequently the copper will be more mobile. This seems more plausible than the other explanation. Under existing conditions it was unfortunately not possible for me to test this point experimentally.

It is not enough merely to consider the adsorption of the dissolved salt or of one of its decomposition products. The taking up of water is an important factor. Vignon[2] has shown that one gram of cotton may take up five grams of water. That is an extreme case and does not occur in any ordinary experiments with filter paper. Suppose, however, that we let fall a drop of solution on a piece of filter paper and suppose that the nature and concentration of the solution are such that water is taken up more rapidly that the dis-

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[1] Skraup: Sitzungsber. Akad. Wiss. Wien, **118**, IIb, 565 (1909).

[2] Comptes rendus, **127**, 73 (1898).

solved substance. In that case a more concentrated solution will spread out and we shall get an outer ring of a concentrated solution.

This was actually observed by Bayley[1] though he was unable to account for the phenomenon. "Experiments with the hydrates of calcium, sodium, and ammonium dropped upon turmeric paper, showed that the water-ring is formed if the solutions are dilute. When they are concentrated, the alkali extends to the edge of the blot and, indeed, seems concentrated there, for the brown patch is surrounded by a ring darker in color than the other parts."

In one place Skraup[2] says that "*N*/50 hydrochloric acid is adsorbed by the same surface of paper more strongly than acetic acid, and consequently it must rise less high in filter paper, which is actually the case." This sounds as though Skraup were fairly clear as to the theory of the phenomenon but the following quotation[3] makes one doubtful whether this is much more than an accidental phrase. It certainly never became a working hypothesis.

"In many cases the difference in the heights to which the solutes rise is approximately as great as the difference in the degree of electrolytic dissociation. That this is not the sole cause of the differences appears from the behavior of sulphuric acid, which rises to about the same height as the halogen acids and nitric acid at concentrations for which it is much less dissociated than these. More remarkable still is the behavior of phosphoric acid which is distinctly a weak acid and yet which rises less high than the strongest acids. Since experiments with the basic hydroxides have shown that barium hydroxide and calcium hydroxide rise less high than the oxides of the alkalies, we might account for the behavior of phosphoric acid by ascribing an important part to valency taken in its broadest sense. As against this

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[1] Jour. Chem. Soc., 33, 306 (1878).

[2] Sitzungsber. Akad. Wiss. Wien, 118, IIb, 596 (1909).

[3] Ibid., 118, IIb, 562 (1909).

we shall have rises with boric and succinic acids. Perhaps a study of other acids will clear up matters.

"With the alkaline hydroxides we have in general the same results as with the acids, the solutes rising less high with increasing dilution. As previously stated, the stronger bases rise higher than the weaker ones. It is interesting to note that at high dilutions the hydroxides, and especially those of the alkalies rise higher than do equivalent concentrations of the strong acids. It is not possible even to guess whether this has anything to do with the fact that transference numbers for hydrogen and hydroxyl vary in magnitude in the opposite direction."

"Ammonia and ethyl amine show an abnormal behavior. Both rise much higher than the strong alkali hydroxides, and the heights to which they rise decrease but little at first with increasing dilution. At a concentration of $N/100$ ammonia rises about as the alkalies. Until other amines have been studied, it is impossible to formulate any definite statement.

"The most striking thing about salts is that in general they rise much higher than equivalent solutions of the corresponding acids and bases. In many cases it is difficult to detect any lagging of the solute behind the water even at high dilutions. Even with those salts which rise to a lesser height with increasing dilution, the rise is higher than that of an equivalent solution of the corresponding base or acid except for extreme dilution. This relatively large rise of the salts is in accord with the observations on the action of salt solutions on porous substances such as bone-black, kaolin, etc., as these substances adsorb salts of the alkalies only to a very slight extent.

"Of special influence on the rise of salt solutions is hydrolysis and this can be detected even with very stable salts. With sodium chloride or potassium sulphate, for instance, the part of the filter paper outside of the solution gave a faint blue color with neutral litmus or azolitmin while the submerged end assumed a faint reddish color when tested. Increasing dilution causes a decrease in the rise in the case of salts which we know to be strongly hydrolyzed. At concentrations greater than *N*/100 potassium carbonate rises higher than potassium hydroxide; but this difference ceases to be perceptible in *N*/200 solutions. This points to practically complete hydrolysis. In fact the degree of electrolytic[?] dissociation can be shown indirectly in many cases. Thus mercuric cyanide, which is scarcely dissociated at all, rises nearly to the same height with increasing dilution, whereas the decrease is much more marked with cadmium iodide, which is more dissociated to start with and, therefore, also more hydrolyzed."

Skraup evidently did not appreciate that the filter paper causes hydrolysis when it tends to adsorb a base more than an acid or vice versa.[1] Shields[2] found that sodium carbonate was about three percent hydrolyzed in *N*/10 solution. It is, therefore, very improbable that potassium carbonate is completely hydrolyzed in *N*/200 solution as Skraup assumes. Kohlrausch[3] gives the equivalent conductivity of *N*/200 K_2CO_3 as 121.6 at 18° and the corresponding value for potassium hydroxide as 230.

Lloyd's experiments[4] are very similar to Bayley's except that he used some mixtures containing three or more dissolved substances. He found that the water-ring is widest the more dilute the solution. Owing to not working with sufficiently dilute solutions he obtained no water-ring with sodium chloride. One experiment is interesting enough to be worth quoting. "In carrying this series of experiments further, it is readily shown that not only can we separate liquids from each other within the paper, but we can separate them as liquids by acknowledging the fact that a liquid tends to flow from a tube, capillary or otherwise, if the extremity is beneath the surface of the liquid in the container. Two

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[1] Bancroft: Jour. Phys. Chem., 18, 6 (1914).
[2] Zeit. phys. Chem., 12, 167 (1893).
[3] Leitvermögen der Elektrolyte, 159 (1898).
[4] Chem. News, 51, 51 (1883).

test-tubes were placed beside each other, and into one an inch of solution of ferric sulphate (the strength before named) was poured. A strip of blotting paper was then so placed that one end reached into the liquid, while the other end rested below it in the other vial. The paper was curved so that the height was four inches; therefore, the liquid traversed eight inches. The exposed part of the paper was covered by means of a sheet of rubber, in order to retard evaporation. In twenty-four hours a layer of colorless liquid was carried into the empty vial, and this liquid refused to show a trace of iron by the usual reagents."

The fundamental difference between the spreading of a drop on filter paper and the rise of a solution in filter is that the solution becomes exhausted in the first case and not necessarily in the second case. If the strips are left in the solution long enough, fresh solution can rise in them, carrying the solute higher. This is shown clearly in some experiments by Pelet-Jolivet[1] with dyes (Table II).

TABLE II

Time of experiment, hours	0.5	1	2	4	6
Methylene blue, 0.1 percent					
Rise of dye, mm	20	24	30	42	47
Rise of water, mm	88	107	152	185	215
Methylene blue, 0.2 percent					
Rise of dye, mm	24	32	49	65	79
Rise of water, mm	83	102	152	185	215
Crystal ponceau, 0.1 percent					
Rise of dye, mm	76	103	121	156	186
Rise of water, mm	91	114	148	195	230
Crystal ponceau, 0.2 percent					
Rise of dye, mm	66	102	124	153	187
Rise of water, mm	79	114	154	195	230

Unless fresh solution is supplied from below, the height to which the solute rises does not vary much with the time. Blotting paper was cut into 8 cm lengths and was dipped

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[1] "Die Theorie des Färbeprozesses," 123 (1910).

into solutions of such concentrations that a water zone was always formed. A known volume of the solution was taken up, usually one cubic centimeter. When all the liquid had been taken up, the strips were set aside in a moist atmosphere for different lengths of time and then the height determined to which the solute had risen. With cadmium sulphate or copper sulphate this was done by exposing the strips to hydrogen sulphide. With 0.05 molar cadmium sulphate and 8 cm strips the cadmium salt stood at a height of 7.4, 7.3, 7.7 and 7.3 cm after an hour in the moist atmosphere and at 7.4 cm after eighteen hours. With 0.025 molar copper sulphate and 7 cm strips, the copper stood at a height of 5.4 ± 0.1 cm at all periods from fifteen minutes up to eighteen hours. Theoretically, there should be a levelling effect and an eventual uniform distribution of the solute; but practically this effect is negligible.

One of the points which excited comment is the sharpness of the dividing line.[1] "Take an ordinary drop of porous blotting paper and drop into its centre some writing fluid drop after drop. The spot will spread, but it will not present the same appearance from the centre outward. There is usually a dark centre, and then a dark line of demarcation, after which another shade appears, which, after spreading to a certain distance, will perhaps suddenly give place to a nearly colorless liquid. Continue to add the fluid slowly to the centre of the blot, and the shades of color will expand and preserve their individuality, but the outer will usually grow more rapidly than the one immediately within. Sometimes several shades will be formed, but their individual characteristics will be maintained. If the ink be one of the purple or other colors of aniline, or a carmine, it will generally be found that the outer liquid will be colorless. The striking feature is the abrupt change from one shade to the other. It is not a gradual grading-off, for a distinct line of demarcation usually separates each shade. We have introduced this experiment

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[1] Lloyd: Chem. News, 51, 51 (1885).

because it can be so readily performed, and because, upon second thought, every person must even now admit its familiarity. Mix two colors of ink, say red and blue, and try the experiment again. Very likely it will be observed that, under the same conditions, one color will leave the other after both have passed together for a certain distance, and leave it completely, and by a distinct line of demarcation. Then, perhaps, this second color will cease to spread, and a colorless liquid will pass out, and form a ring encircling the ink spot."

The reason for the sharp dividing line is apparent when we consider the form of the adsorption isotherm. In most cases the amount adsorbed increases very rapidly with small increases in the concentration of the solution. Consequently the range of gradations will be correspondingly narrow and will usually escape notice. If one had a substance which gave a much flatter adsorption curve with cellulose, one would not get the apparently sharp dividing line. While it would be interesting to have such a case, I have not been able to devote any time to searching for a suitable substance. It would, of course, be one for which the exponential factor was low in the equation for the adsorption isotherm.

Pelet-Jolivet[1] has studied the rise of dyes in filter paper and in other fibers. "It is not possible to explain each one of the results satisfactorily. Nevertheless we can deduce from them a certain number of general rules which are very interesting.

"1. For a given fiber the rise of a dye is less the more readily the dye is adsorbed by the fiber.

"2. If a dye is adsorbed by a fiber, the capillary rise is generally less for dilute concentrations and greater for high concentrations. A graphical representation of the relation between rise and concentration gives a curve which bears a strong resemblance to adsorption curves.

"3. Basic dyes rise to a moderate height but usually not so high as acid dyes; rhodamine dyes, which are less basic,

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[1] "Die Theorie des Färbeprozesses," 128 (1910).

come in between these two classes. Direct cotton colors usually rise less high than the acid colors. Among the basic colors those containing NH_2 groups usually rise less high in cellulose (paper and linen) than those containing $N(CH_3)_2$ or $N(C_2H_5)_2$ groups. This difference does not occur with animal fibers.

"4. Dyes having a distinctly marked colloidal character usually rise less high than others (fuchsine, alkali blue, benzopurpurine) of similar constitution.

"According to a still unpublished paper[1] of which my colleague, Professor Fichter, of Basel, very kindly informed me, it seems certain that changes in the capillary rise depend to some extent on the colloidal state. He has studied the rise of positive and negative colloids in strips of paper and has found that positive colloids rise but slightly while negative colloids rise freely. These interesting facts bring out a new analogy between dyes and colloids although it has been shown that dyes are electrolytes.

"Has the basic or the acid character of the molecule alone an effect on the rise? This seems improbable. There must be other properties which affect the capillarity. With dyes of similar constitution the molecular weight appears to be an important factor, as for instance

	Mean rise Mm
Fluoresceine	151
Eosine (tetrabromfluoresceine)	121
Rose Bengale (dichlortetrabromfluoresceine)	114

"If we sum up these general rules we may say that, subject to the limited accuracy of the method, *the capillary rise and the adsorption are closely connected; the capillary rise is less the greater the adsorption and vice versa.*"

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[1] Fichter: Verh. naturforsch. ges. Basel, 21, 1 (1910); Zeit. Kolloidchemie, 8, 1 (1911).

This final conclusion is entirely right; but it can be interpreted in several ways and the context shows, I think, that Pelet-Jolivet intended merely to say that adsorption was one of the factors and not that it was the factor. He discusses the questions of the molecular weight, of the constitution, of the basicity and acidity, with reference to the capillary rise and not with reference to the adsorption, which is where they belong. He apparently accepts Fichter's views that the precipitation of a positive colloid is fundamentally different from adsorption. Working with dilute solutions, Pelet-Jolivet did not observe the formation of a darker outer zone and he does not refer to the work of others who have observed this. It would have been impossible for him to have accounted for this phenomenon so long as he considered only the adsorption of the solute. The question is one of the relative adsorption of solvent and solute.

There is still a great deal of work to be done before all the details of the rise of solutions in filter paper have been cleared up. We need more facts in regard to specific adsorption and there is also the problem of the movement of water or of solution through the fiber instead of over the surface. It all comes back, however, to a question of adsorption of water and of the constituents of the solution by the paper.

The general results of this paper are:

1. Filter paper shows selective adsorption for water and for each constituent of the solution.

2. If the solute is adsorbed relatively faster than the water there will be formed a water-ring.

3. If the water is adsorbed relatively faster than the solute, the latter will concentrate in the outer zone.

4. Whether one gets a dilute solution (water-ring) or a more concentrated one in the outer zone depends on the concentration as well as on the nature of the solute.

5. The more readily a salt is adsorbed relatively to the water, the higher will be the limiting concentration giving a water-ring.

6. The amount of base or of acid taken out of a salt

solution by filter paper is not a measure of the degree of hydrolysis before the paper was dipped into the solution.

7. Hydrolysis is not complete in a $N/200$ potassium carbonate solution.

8. Since adsorption decreases with rising temperature, the water-ring will be relatively narrower at higher temperatures; the salt will appear more mobile.

9. Addition of anything which cuts down the adsorption —sulphuric acid to copper sulphate solution, for instance—increases the mobility of the salt.

10. With a strip of filter paper dipping into an excess of solution there will be a continual supply of solution to the filter paper, which will give rise to phenomena which we do not get when the filter paper is present in excess, as in the case of a drop of solution upon a piece of filter paper.

11. Theoretically, there should be a tendency for the dissolved substance to distribute itself uniformly over a short strip of filter paper in time. Practically this tendency is negligible.

12. The apparently sharp dividing line in the case of a water-ring is a necessary consequence of the usual form of the adsorption isotherm. With a flatter adsorption isotherm the contrast would not be so marked.

This work was suggested by Professor Bancroft and has been carried on under his supervision.

Cornell University

SOME ADSORPTION PHENOMENA IN SOILS AND KAOLIN[1]

BY J. E. HARRIS

The problem of soil acidity has been for a great many years a serious one for the farmers of the eastern and middle western states and is becoming more serious as the years go by. As the soil continues to be worked, larger and larger areas are found to be sour or acid in character. These soils when moistened and tested with litmus will very quickly turn blue litmus paper red. The peculiar thing about this reaction is that the test paper must be brought into direct contact with the soil particles to bring about the change in color. If the soil, giving the acid action, be shaken with water and the solution thus obtained be decanted off from the soil and tested with litmus, the solution is found to be neutral. Whatever it is that gives the acid reaction, when the test paper is brought into direct contact with the soil particles, is not soluble in water.

These acid soils possess another peculiar property. As above mentioned, if an acid soil be shaken with water, the solution obtained is neutral; but if, instead of water, a solution of a neutral salt be used, such as potassium nitrate, it will be found to contain considerable quantities of a soluble acid.

It is well known that soils that show the above properties are not fertile, and for this reason these soils have been the subject of much investigation. Two explanations have been offered for the behavior of such soils toward indicators and toward solutions of neutral salts. For many years the accepted explanation was this: in acid soils there exist complex insoluble acids called humic acids; these acids being insoluble, of course can not affect litmus until the paper is brought into

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[1] The greater part of this work was carried out in the chemical laboratory of the Michigan Agricultural College Experiment Station at East Lansing, Mich. A few of the experiments were performed in the chemical laboratory of the University of Michigan.

direct contact with the soil particles. To explain the action of the acid soils toward neutral salt solutions, those who accept the humic acid theory maintain[1] that the difficultly soluble acid enters into a double decomposition with the salt in solution thus setting free a certain amount of soluble acid. It is further maintained that by treating the soil with one quantity of salt solution after another, until the soil no longer sets free any acid in the salt solution, the acidity of the soil may be determined, this being measured by the total amount of acid set free in the successive applications.

Of late years, however, this theory has come to be discredited in the minds of a great many chemists and a new theory has been put forward to explain the peculiar behavior of acid soils. Linder and Picton[2] and later Whitney and Ober[3] have shown that when arsenic trisulphide in colloidal solution is precipitated by a solution of barium chloride, the precipitation is accompanied by the adsorption of a slight amount of the barium and that there is set free in the solution a corresponding amount of hydrochloric acid. F. K. Cameron[4] has pointed out that certain substances have a selective absorbing power. For example, metallic silver can be separated from a solution of silver nitrate by the selective adsorbing power of charcoal. Moist cotton, absolutely free from any soluble acid, if left in contact with a piece of blue litmus paper for some time, will redden it. This phenomenon can be explained by ascribing to the cotton a selective adsorbing power for the base of the blue litmus salt, the base being adsorbed leaving the red acid dye on the paper. The action of an acid soil toward litmus may be explained in exactly the same way. Also in the case of the action of the soil toward salt solutions, we may assume that the soil adsorbs the base in exactly the same way that the arsenic trisulphide adsorbed the barium in Linder and Picton's experiment, leaving a

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[1] Bulletin 107, U. S. Dept. Agriculture, p. 20.

[2] Jour. Chem. Soc., 67, 63 (1895).

[3] Jour. Am. Chem. Soc., 23, 842 (1901).

[4] "The Soil Solution," p. 66. The Chemical Publishing Co.

corresponding amount of acid in solution. For example, if an acid soil were treated with a solution of sodium chloride, it would adsorb a certain amount of sodium hydroxide leaving hydrochloric acid in solution. The fact that there is so much colloidal matter in soil makes this theory seem the more reasonable since, as mentioned above, Linder and Picton have shown that the coagulation of negatively charged colloids is accompanied by the adsorption of the positively charged ion. Coehn[1] has come to the conclusion that those colloids which have a lower dielectric constant than water will be charged negatively, while those having a higher dielectric constant will be charged positively. Since, in general, solids have a lower dielectric constant than water, suspension colloids such as we have in the case of soils will be charged negatively and therefore will adsorb the base when coagulated by a salt solution, leaving an acid in solution. This agrees with the facts set forth above.

As stated above, the humic acid theory was at one time quite generally accepted, but of late years the selective adsorption theory has been gaining ground rapidly. In 1910, Baumann and Gully[2] published an article describing some experiments as a result of which they came to the conclusion that the acid action of peat moss and of peat soils in general is caused by colloidal matter present in the cell covering of the hyalin sphagnum cells. This work has been criticized by the adherents of the humic acid theory, especially by Tacke and Süchting,[3] who show that acid soils develop hydrogen when brought into contact with iron, invert sugar, and cause many reactions to take place which can be brought about only by true acids according to Tacke and Süchting. Gully,[4] in a reply to this criticism, asserts that all the reactions mentioned by Tacke and Süchting can be brought about without the presence of any true acid.

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[1] Wied. Ann., 64, 217 (1898).

[2] Mitteilung der K. Bayr. Moorkulturanstalt, 1910, 31–156.

[3] Landw. Jahrbücher, 41, 717–754 (1911).

[4] Mitteilung der K. Bayr. Moorkulturanstalt, 1913, 85.

Be that as it may, the acid reaction of the sand and clay soils of this country could hardly be ascribed to the presence of these hyalin cells. The experiments described in this paper were carried out to determine if possible whether the acidity of these sand and clay soils is caused by the presence of humic acids or by the selective adsorption of bases by the colloidal matter present.

In Bulletin 107 of the Department of Agriculture[1] is given a provisional method for the quantitative determination of acidity in soils. This method is based on the theory, mentioned above, that when a soil is shaken with a neutral salt solution, the difficultly soluble humic acids enter into a double decomposition with the salt thus setting free a soluble acid. The soil is shaken with one portion of salt solution after another until it no longer gives an acid solution. The soil is then found to be neutral toward litmus and the total amount of acid set free is taken as a measure of the acidity of the soil. If the hypothesis upon which this theory is based furnishes the correct explanation for the action of the soil, then the soil should give the same amount of acid no matter what salt solution is used. On the other hand, if the action is due to selective adsorption on the part of the soil, we would expect the amount of adsorption to depend more or less on the salt used, since colloidal substances will adsorb more of some bases than of others. To determine whether or not the same amount of acid is set free when different salt solutions are used, samples of a soil were treated with solutions of potassium nitrate, sodium acetate, and sodium chloride. The method of procedure was to weigh out 100 grams of soil and to add to this 250 cc of the salt solution used. Each of the three salt solutions was made up normal. The solution was left in contact with the soil for a period of from two to three hours, the mixture being frequently shaken. The soil was centrifuged and a 100 cc test portion drawn off and titrated with $N/50$ alkali. The re-

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[1] Loc. cit.

mainder of the solution was then poured off from the soil and the treatment repeated. From the amount of alkali required to neutralize the acid in the test portion, the total that would be required to neutralize all the acid set free after each addition was computed. The treatments were continued until the amount of acid found in the test portions was very small and the soil samples were no longer acid toward litmus. The results of the experiment are shown in Table I.

TABLE I

No. of treatment	KNO_3 Cc	$NaC_2H_3O_2$ Cc	NaCl Cc
1	41.0	98.0	27.3
2	8.7	32.1	9.3
3	5.4	23.2	6.4
4	3.7	17.2	3.9
5	3.2	14.5	3.3
6	2.8	13.0	2.6
7	2.2	12.0	2.2
8	1.9	11.3	1.8
9	1.6	11.0	1.8
10	1.3	10.7	1.6
Total	71.8	243.0	60.2

In the above table is given the amount of $N/50$ alkali that corresponds to the amount of acid set free by each of the three soil samples with each successive addition of salt solution. It is seen from the table that the greatest amount of acid is set free in the sodium acetate solution, the potassium nitrate coming next and the sodium chloride last. The important thing to be noticed is that not only is a much greater amount of acid set free in the sodium acetate solution than in the potassium nitrate solution, but that the ratio of the number of cubic centimeters set free in the former case to that in the latter becomes greater with each successive application. Thus we see that the ratio of the acid set free in the first application of sodium acetate to the corresponding number for the potassium nitrate is 2.39, while the ratio of the totals in the two cases is 3.38. The ratio in the case of the last applications is 8.2. These values indicate that not only do we not get the same amount of acid liberated in the salt solutions, but that the difference in amounts becomes greater with each succeeding application of salt solution. Thus we find that the facts do not fit in with the humic acid theory but do satisfy the conditions of the selective adsorption theory. The above results also indicate that those methods for the quantitative determination of the acidity of the soil that depend upon the treatment of the soil with a neutral salt solution are valueless, unless the same substance that is actually made use of in the field for correcting the acidity is also made use of in the determination. It is probable that the methods of Veitch[1] and of Süchting[2] would come closest to giving the true lime requirement of the soil, since the former employs lime water and the latter calcium carbonate as the reagent in the determination.

Experiments similar to those above were performed with other samples of soil and always with the same result; the greatest amount of acid being set free in the sodium acetate solution, a very much smaller quantity in the potassium nitrate solution, and least of all in the sodium chloride solution.

Assuming for the time being that we do have selective adsorption on the part of the acid soils, how are we to explain the fact that all soils are not acid although they all contain colloidal matter? Also why is it that soils that were originally alkaline or neutral come in time, after long cultivation, to show acid properties? These questions may be easily answered in the light of the selective adsorption theory. We may assume that in all soils in the uncultivated condition there is enough basic material, especially lime, to cause the colloidal matter to be present in the flocculated condition. However, as the soil lies in contact with the decaying organic matter, the organic acids thus formed gradually neutralize the bases

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[1] Jour. Am. Chem. Soc., 24, 1120 (1902).

[2] Zeit. angew. Chem., 21, 151 (1908).

present forming soluble salts which may be washed out. Also the growing crops themselves will remove considerable quantities of the bases. Under the action of these two agencies, the soil will after a time become deficient in basic material and will adsorb the basic material from any neutral salt with which it comes in contact. If this be the manner in which soils become acid, it is probable that all the basic matter is not removed by the above process. The soil must obviously be able to retain some of the basic matter in the presence of very dilute acids, for otherwise the soil could not adsorb the base from a neutral salt and hold it adsorbed in the presence of the acid thus set free. This being the case, it is probable that the addition of a fairly dilute acid to the soil would largely increase its acidity, due to the fact that the bases still present in the soil would by this process be neutralized and could then be washed out.

To determine if this were the case, a 100 gram sample of an acid soil was treated with *N*/20 sulphuric acid and washed, using a porcelain filter, until the wash water was practically neutral. For comparative purposes, samples of kaolin and of exceedingly finely ground quartz sand were treated in the same way. The samples were left in contact with the acid for about twenty-four hours in each case. After washing, each sample was shaken with 250 cc of a normal solution of potassium nitrate. 100 cc test portions were then drawn off and titrated. 100 gram samples of each of the materials that had not been previously treated with an acid were also shaken with potassium nitrate solution and the acid set free titrated in the same way. In the following table are shown the quantities of *N*/50 sodium hydroxide that were required to neutralize the acid set free in each 100 cc test portion:

TABLE II

	Cc $N/50$ NaOH
Soil untreated	1.0
Soil treated with $N/20$ H_2SO_4	9.1
Kaolin untreated	0.0
Kaolin treated with $N/20$ H_2SO_4	7.4
Sand untreated	0.0
Sand treated with $N/20$ H_2SO_4	0.0

It will be seen from the above table that the acidity of the soil was very much increased by the treatment with acid just as we must expect it to be if we are to accept the explanation given above for the acidity of the soil. The unexpected, however, was encountered in the case of the kaolin. The kaolin in its original state was perfectly neutral in its action toward salt solutions. But after its treatment with the acid, and after the soluble acid had been carefully washed out, the kaolin was found to act in a manner similar in every respect to the acid soils. It reddened blue litmus when the paper was brought into direct contact with the solid particles of kaolin, and when shaken with a solution of potassium nitrate, appreciable quantities of acid were set free as is shown in the above table. The finely divided sand gives no appreciable effect either before or after the treatment with acid.

To determine the effect of different acids on the soil and kaolin, several hundred grams of each of these substances were treated with solutions of $N/20$ HCl, H_2SO_4, $HC_2H_3O_2$, and $H_2C_2O_4$. The soil was then thoroughly washed until the wash water was neutral, and three 100 gram portions of each of the above samples were taken, one of these being treated with a normal solution of potassium nitrate, and another with a solution of sodium acetate, and the third with sodium chloride. The results of these experiments are shown in Table III. 250 cc of salt solution were used in every case. The table gives the quantities of $N/50$ sodium hydroxide required to neutralize the acid set free in 100 cc test portions of the salt solutions.

TABLE III

	KNO_3 Cc	$NaC_2H_3O_2$ Cc	NaCl Cc
Soil untreated	16.0	36.0	9.5
Soil treated with *N*/20 H_2SO_4	24.3	45.0	19.0
Soil treated with *N*/20 HCl	23.5	46.5	18.0
Soil treated with *N*/20 $H_2C_2O_4$	19.5	46.8	15.0
Soil treated with *N*/20 $HC_2H_3O_2$	19.0	42.5	14.6
Kaolin untreated	0.0	0.0	0.0
Kaolin treated with *N*/20 H_2SO_4	8.1	16.0	7.5
Kaolin treated with *N*/20 HCl	7.4	14.3	6.6
Kaolin treated with *N*/20 $H_2C_2O_4$	4.6	11.8	4.1
Kaolin treated with *N*/20 $HC_2H_3O_2$	6.4	13.4	5.5

It is to be noticed from the above table that the effect of the acid in each case is to increase largely the power for adsorption in the soil and kaolin, just as we found that it did in the experiment the results of which are given in Table II. The amount of increase seems to be of about the same degree of magnitude in the case of the different acids, the two weaker acids, oxalic and acetic, giving somewhat less effects than the hydrochloric and sulphuric acids. It is seen that the three salt solutions stand in the same order with respect to the amount of acid set free in the case of the untreated soil, that of the soil treated with acids, and in the case of the kaolin that had been treated with acids. This would indicate that, whatever it is that causes the liberation of the acid, we have a similar phenomenon in the three cases. It is impossible to suppose that we have any humic acid in the case of the kaolin or for that matter any other true acid. Since the soil acts in every way like the kaolin, it is fair to assume that the cause of the action toward litmus and toward salt solutions is similar in the two cases, and is not due to the presence of humic acids.

There is another possible explanation for the action of the soil and kaolin. It is possible that the soil and kaolin adsorb the acid with which they come in contact and hold it in an insoluble condition and that the effect of the salt solution is to set the acid free either by a double decomposition or by some physical action on the soil particles. For example, the soil might have a greater adsorptive power for the salt than for the acid, and in taking up the salt from the solution the acid might be set free. Such an action would not be surprising since van Bemmelen[1] has shown that a silica gel of the composition $SiO_2.4H_2O$ will retain aluminium chloride so tenaciously that it can not be washed out, but if the gel be brought into contact with a solution of potassium chloride, considerable quantities of the latter are adsorbed and a large part of the aluminium chloride goes into solution. If something of this nature happens in the case of the soil, it is likely that there would be a great variation in the amount of acid adsorbed if the concentration of the acid with which it is brought into contact were varied. If, on the other hand, the effect of the acid is to neutralize the bases already present, rendering the soil capable of adsorbing greater quantities of the bases of the salt solutions with which it comes in contact, we would not expect any great variation until an acid so dilute is used that the soil could hold the base adsorbed in spite of the action of the acid. This would have to be an acid nearly as dilute as that found in the salt solution after being shaken with the soil. To determine the effect of concentration of the acid on the absorptive capacity of the soil, samples of a soil were treated with solutions of $N/2$, $N/5$, $N/10$, $N/20$, $N/40$, and $N/80$ sulphuric acid, washed and treated with a normal solution of potassium nitrate, 100 cc of this being titrated as in the previous experiments. Table IV shows the amount of $N/50$ sodium hydroxide required to neutralize the acid found in the 100 cc test portions in each case. The same experiment was carried out with kaolin.

TABLE IV

	Untreated Cc	$N/2$	$N/5$	$N/10$	$N/20$	$N/40$	$N/80$
Soil	14.8	26.8	29.5	28.3	29.9	28.6	25.8
Kaolin	0.0	18.3	18.5	18.1	16.9	16.1	13.4

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[1] Jour. prakt. Chem., [2] 23, 324–349, 379–395 (1881).

In the above experiment the kaolin used was from a supply different from that of the preceding experiment. It will be seen from the above results that the concentration of the acid did not have any great effect on the adsorptive power of the soil. What variation there is seems to be due to a variation in the different samples of soil used, since it was impossible to get samples that were absolutely homogenous. This would indicate that we do not have any adsorption of the acid by the soil because there is no appreciable decrease in effect with decrease in concentration of the acid. It would seem that the effect of the acid is merely to neutralize the bases already held adsorbed, thus increasing the capacity for adsorption of the base from the salt solution. On the other hand, there is a marked falling off in effect with decrease of concentration in the case of the kaolin. It may be in this case that the effect of the acid is not so much to neutralize the bases already present as it is to change by a chemical reaction the silicates of the kaolin into compounds that can selectively adsorb the base of the salt.

That there is no adsorption of the acid by either the soil or the kaolin was further proven by treating samples of soil and of kaolin with $N/20$ sulphuric acid, washing until practically free from soluble acids, and then treating with a normal potassium nitrate solution. If any acid had been adsorbed by the soil or kaolin, it would have to be set free by the action of the salt solution in order to account for the free acid present in that solution. On testing for the presence of the sulphate radical in the potassium nitrate solution, only a minute trace was found, the amount being sufficient to account for a very small fraction of the acid found in the solution. This means that whatever the free acid was in the potassium nitrate solution, it was not sulphuric acid. Therefore the action of the soil and of the kaolin on the salt solution could not have been caused by the presence of sulphuric acid held adsorbed by those substances.

To determine whether the base is actually adsorbed from the salt solution or not, a sample of soil and a sample of kaolin were treated with *N*/20 hydrochloric acid and washed until the wash water was practically neutral. The samples were next treated with 250 cc of normal barium chloride solution and 100 cc test portions titrated with *N*/50 sodium hydroxide. The soil and kaolin were then washed until practically free from barium salts, when they were again treated with *N*/20 hydrochloric acid. 100 cc test portions of this acid solution were then drawn off and treated with sulphuric acid to precipitate the barium salts. Blanks were run to correct the weight of barium sulphate since it was found very difficult to wash out all the soluble barium salts previous to the second treatment with the acid. After the second treatment with acid, the soil and kaolin were again washed and a second time treated with a solution of barium chloride. The results of the experiment are shown in Table V.

TABLE V

	Cc *N*/50 NaOH in first $BaCl_2$ solution Cc	Wt. of $BaSO_4$ g	Cc *N*/50 NaOH calc. from wt. of $BaSO_4$ Cc	Cc *N*/50 NaOH in second $BaCl_2$ solution Cc
Soil	27.7	0.0631	26.3	30.4
Kaolin	12.5	0.0259	11.1	8.6

In the above table, the first column indicates the amount of *N*/50 sodium hydroxide required to neutralize the acid set free in a 100 cc test portion of the first barium chloride solution. The second column shows the weight of barium sulphate that was recovered from a 100 cc test portion of the acid with which the samples were treated after the barium chloride had been applied. The weights given in that column have been corrected for the weight of barium sulphate found in the blanks. The third column indicates the number of cc of *N*/50 sodium hydroxide corresponding to the weight of barium sulphate recovered. The last column indicates the amount of *N*/50 sodium hydroxide required to neutralize the acid set free when the soil and kaolin were treated a second time with barium chloride solution.

From this table we gain the following information: First, the barium in one form or another is taken from the solution of barium chloride and held by the soil and the kaolin in an insoluble condition; second, the barium is rendered soluble by the treatment with dilute hydrochloric acid; third, that the amount of barium recovered by this treatment with hydrochloric acid corresponds very nearly to the amount of acid set free in the barium chloride solution, the amount of barium sulphate recovered corresponding to 95 percent of the acid set free in the case of the soil and to 89 percent in the case of the kaolin; fourth, after the second treatment with hydrochloric acid, the soil was rendered capable of setting free a slightly greater amount of acid than it was after the first treatment, and the kaolin, although the amount of acid obtained in the second application of the salt was less than in the first, was rendered capable of liberating a much greater quantity of acid in the second treatment than it would have been capable of had it not in the meantime been treated with an acid. Both the soil and the kaolin were rendered capable by the second treatment with the acid of abstracting much more of the barium from the barium chloride solution than they would have had this second treatment with acid been omitted. A second treatment of the soil or kaolin with a salt solution usually gives from a third to a fifth as much acid as the first treatment.

The selective adsorption theory furnishes a satisfactory explanation for the above facts. We may suppose that the first treatment with hydrochloric acid removes the bases, held adsorbed by the soil in its natural condition, by neutralizing them and converting them into soluble salts. The soil being then shaken with a solution of barium chloride, adsorbs barium hydroxide from the solution, setting free a corresponding amount of hydrochloric acid. The second treatment with acid neutralizes the barium hydroxide converting it into the soluble chloride which is washed out. As the table shows, the amount of barium sulphate recovered corresponds almost quantitatively to the amount of acid liberated in the salt solution. This removal of the barium hydroxide leaves the soil in just the same condition that it was in before the first addition of barium chloride, so that when the barium chloride is added a second time, about the same amount of acid is set free as in the first case.

The facts set forth above can not be explained satisfactorily by the humic acid theory. According to that theory, the acid acts by a double decomposition with the salt setting free an acid. The following reaction would represent the change:

$$HA + BaCl_2 \longrightarrow BaA + HCl$$

A large part of the humic acid, HA, must be transformed by this process into the salt, BaA, because the first addition of a salt always gives a much greater quantity of acid than the next application, and if the applications are continued until the soil is practically neutral, it is found that the acid set free in the first application is a large percentage of the total. If we are to accept the law of mass action, this means that, for the action to go as far as it does, the salts of the humic acids must be either far more insoluble or far less dissociated than is the humic acid. To account for the recovery of the barium by the treatment with hydrochloric acid, the reverse action

$$BaA + HCl \longrightarrow BaCl_2 + HA$$

must take place, and since 95 percent of the barium taken up by the soil is recovered by this process, the reaction goes almost to completion in this reverse direction. For the reaction to go so nearly to completion in this direction, the humic acid must be far more insoluble or far less dissociated than the barium salts of these acids. But this conclusion is the exact reverse of that reached as a result of the first reaction. As a result of the above experiment we must conclude that we do not have a case of double decomposition, and that the action of the soil is due to selective adsorption.

It was noticed in titrating the salt solutions with which the soil had been treated that the addition of the alkali was accompanied by the separation of a light brown gelatinous precipitate. It was also noticed that a similar precipitate separated out in the corresponding experiments with the kaolin, except that the precipitate in this case was white. At first it was supposed that the precipitate in the case of the soil consisted, at least in part, of organic matter. However, when tested, it was found that the precipitate was wholly inorganic and consisted of a mixture of ferric and aluminium hydroxides. In the case of the kaolin, the precipitate was almost entirely aluminium hydroxide. These facts together with the similarity of behavior of the soil and kaolin that had been treated with an acid, raised the question as to what extent the selective adsorptive power of the soil is due to organic colloidal matter and to what extent it is due to inorganic. To determine this, a 100 gram sample of the same kind of soil that was used in the experiment of Table IV was boiled for six or seven hours in concentrated sulphuric acid in a Kjeldahl flask. This entirely destroyed the organic matter leaving a clean white sand. The soluble acid was washed out and the soil treated with a normal solution of potassium nitrate. A 100 cc test portion was drawn off and titrated. It was found that 29.1 cc of $N/50$ sodium hydroxide were required to neutralize the acid set free in the salt solution. It will be noticed from Table IV, that the corresponding values for samples of this soil treated with acid varying in strength from $N/2$ to $N/80$ extended from 25.8 to 29.9 cc. We have then a soil quite free from organic matter with a power to affect a salt solution in almost exactly the same degree as the soil with all the organic matter present.

The above experiment indicates that not only is the peculiar behavior of the soil not due to the presence of insoluble organic acids, but that it is not due to the presence of organic matter at all but to inorganic compounds, probably hydrated silicates. This conclusion is in agreement with facts observed by many other investigators. As long ago as 1850, Way[1] succeeded in producing a silicate of sodium and

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[1] Jour. Roy. Agri. Soc., 11 (1850).

aluminium that would adsorb ammonia from a water solution. This experiment is not, however, strictly analogous to those described above, because we do not have in this case the colloidal matter breaking up a salt and setting free an acid. It does show, however, that substances of this nature very readily adsorb basic compounds. Dumont[1] has shown that clay, silicic acid, and ferric hydroxide will react with potassium carbonate and liberate carbon dioxide. Kaolin he found to be practically inactive toward the salt. The latter result is in agreement with the results of the writer since he found kaolin to be inactive toward a salt solution until it had been treated with an acid. Kozai[2] makes the statement that a soil had been investigated by Daikuhaira which was quite free from humus although acid in its action toward salt solutions. No data are given in this article, but a publication on the investigation of the soil is promised. The writer has searched the literature but has been able to get no trace of the promised article.

Summary

It has been found that acid soils of the sandy loam type liberate different quantities of acids in different salt solutions and that the quantities of acid liberated in successive applications of the different salt solutions do not tend to approach the same limiting values, but that the differences become greater with each successive application of salt solution. When sodium acetate, potassium nitrate and sodium chloride are the salts used, it is found that they stand in the order written with respect to the amount of acid liberated. These results indicate that the acid in the salt solutions is not liberated by any double decomposition with insoluble organic acids of the nature of humic acids, but through the adsorption of the base of the salt, the amount of base adsorbed depending on the salt used. The adsorption is of course accompanied by the liberation of a corresponding amount of acid.

If a soil be treated with a dilute acid and washed until

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[1] Comptes rendus, 142, 345 (1906).

[2] Chem. Zeit., 32, 1187 (1908).

the soluble acid is removed, the power of the soil for setting free an acid in a salt solution is greatly increased. This fact may be explained by supposing that the acid neutralizes and converts into soluble salts the basic material held adsorbed by the soil in its natural condition, thus rendering the soil capable of adsorbing larger quantities of the base when brought in contact with a salt solution. These results throw some light on the process by which soils, that were originally neutral or slightly alkaline, come in time under constant cultivation to be acid in character.

Kaolin in its natural condition does not affect a salt solution. But if it is first treated with an acid, the soluble acid being then washed out, the kaolin is found to have a very sharp acid action toward blue litmus and to have the power of liberating an acid from a salt solution in exactly the same way that a soil does. Further, when the kaolin is treated with solutions of sodium acetate, potassium nitrate, and sodium chloride, it is found that these substances stand in the same order with respect to the amount of acid liberated as they do in the case of the soil.

Soil treated with solutions of sulphuric acid varying in concentration from $N/2$ to $N/80$ is found to be affected in almost exactly the same degree. This gives further confirmation of the theory that the effect of the acid is to neutralize and remove the bases held adsorbed by the soil in its natural condition. If this is the effect of the acid, the concentration would not matter unless the acid were so dilute that the soil could hold the base in the presence of the acid, as it does when it adsorbs the base from a salt and holds it in the presence of the acid set free.

Kaolin, treated with solutions of sulphuric acid of the same concentration as those used in the case of the soil, is affected differently by the different concentrations, the effect decreasing with decrease in concentration of the acid. That the kaolin acts differently from the soil in this regard, may be due to the fact that the effect of the acid is not so much to remove basic matter held adsorbed by the kaolin as it is to transform by chemical action some of the silicates into colloidal compounds which have the power to selectively adsorb the base of any salt with which they come in contact.

That the acid is not adsorbed by the soil and kaolin and liberated again when treated with a salt solution, was shown by treating samples of soil and kaolin with sulphuric acid, washing out the acid and treating with potassium nitrate solution. Although a soluble acid was set free in the potassium nitrate solution, no evidence of the presence of the sulphate radical could be found. This showed that there had been no adsorption of the acid.

To show that the base of the salt is actually adsorbed by the soil and kaolin, samples of these substances were treated with dilute hydrochloric acid, and then with a barium chloride solution, the amount of acid that was set free in the solution being determined. The soil and kaolin after being thoroughly washed were treated again with hydrochloric acid and the amount of barium recovered by this process determined. It was found that the barium recovered in the case of the soil corresponded to 95 percent of the acid liberated in the barium chloride solution and to 89 percent in the case of the kaolin. The soil was found after this second treatment with hydrochloric acid to have regained all its original capacity for liberating an acid from a salt solution.

Finally it was found that a soil which had been boiled for six or seven hours with concentrated sulphuric acid to remove the organic matter, after being washed to remove the soluble acid, had the power of setting free almost exactly the same quantity of acid from a salt solution as a sample of the same soil which had been treated with $N/20$ or $N/40$ acid and in which all the organic matter was present. This would indicate that acid soils of the sort investigated (sandy loams) owe their acidity not to organic matter but to inorganic matter, probably to hydrated silicates.

ELECTRODEPOSITION OF NICKEL

BY C. W. BENNETT, H. C. KENNY AND R. P. DUGLISS

A number of years ago, Calhane and Gammage[1] published some very interesting facts concerning the deposition of nickel from solutions of nickel ammonium sulphate. Although these experiments were made to study the impurities such as iron, deposited with the nickel, they bring out some facts which may serve to throw light on the theory of nickel deposition.

In their work, the anodes used were the commercial ones, containing about 7.5 percent iron, and about 92 percent nickel. The first experiment consisted in the electrolysis of the nickel solution (containing about 80 grams of nickel ammonium sulphate per liter of water) using the nickel-iron anodes and platinum sheet cathodes. The current density was about 4 amperes per square decimeter, and the current efficiency on a one-hour run, was about 88 percent, the deposit containing about 0.15 percent iron. The effect of stirring was then tried by running two cells in series, one having a stirrer which rotated 130 revolutions per minute, while the other had a stationary electrolyte. The efficiency in the two cells was practically the same, being about 90 percent. The iron in the deposit from the still solution was 0.13 percent, and that from the stirred solution was 0.36 percent. The effect of rotating the cathode was then tried by running two cells in series, the conditions being the same with the exception that one held a stationary cathode while the other had the cathode rotated 130 revolutions per minute. The efficiency of deposition was 91 percent with the stationary and 12 percent with the rotating electrode. The iron contained in the deposit was 0.11 percent for the stationary, and 0.55 percent for the rotating cathode. Cathodes were used rotating 260, 519, 1041, and 2160 revolutions per minute, and

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[1] Jour. Am. Chem. Soc., 29, 1268 (1907).

efficiencies of 69, 65, 55, and 40 percent, respectively, were obtained.

Unless the anodes were enclosed in bags, or the cathode placed in a porous cup, the iron content of the rotating cathode was always greater than that of the stationary ones.

In view of the fact that nothing has appeared, since this publication, to explain the seemingly specific effect, due to the rotation of the cathode, it was thought that an explanation should be sought with the idea of explaining some other facts found with rotating cathodes. Interest was also stimulated by the recent symposium on electroplating.

In checking up the work of Calhane and Gammage, the following curves of efficiency were obtained, which are plotted against time in minutes as ordinate. By running for fifteen minutes and weighing, and then continuing, the effect of time is shown very plainly. The rotating cathode shows a lower efficiency than the stationary. The solution used contained about 7 grams of crystallized nickel ammonium sulphate, and 1 gram of nickel chloride per 100 cc of water. The anodes contained about 0.75 percent of iron. The current density was 1.5 amperes per square decimeter. The run giving the third curve at the top of Fig. 1, was made with a solution

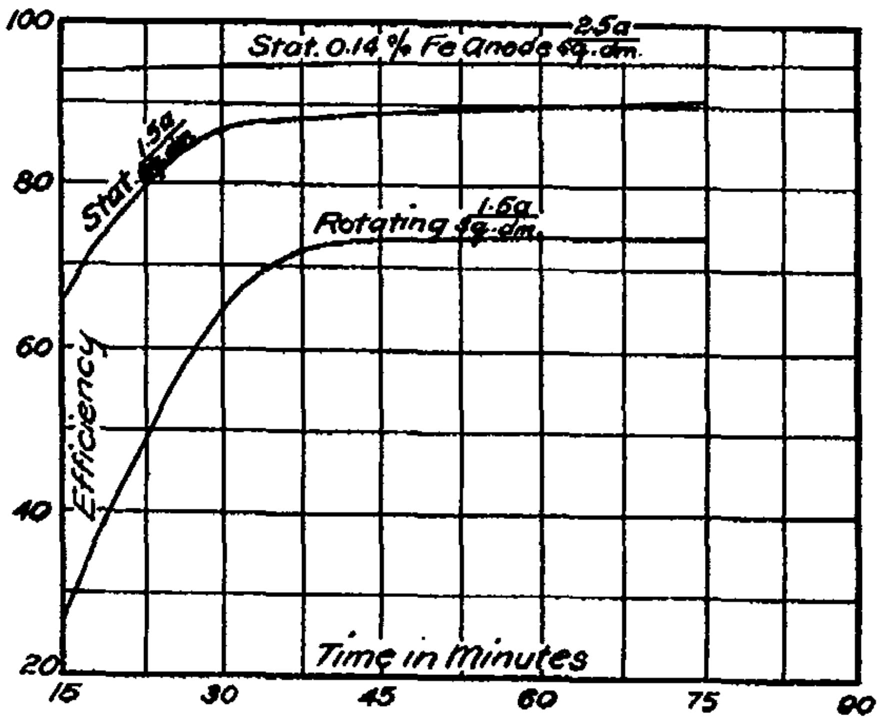

Fig. 1

containing 8 grams nickel ammonium sulphate crystalline, and 1 gram nickel chloride per 100 cc of water. The anode was 0.14 percent iron, the current density was about 3 amperes per square decimeter. Here the anode having the least iron content is in the cell which gives the highest efficiency. It was therefore thought that iron had something to do with the lowering of the efficiency. Attempts were made to obtain pure nickel plate which contained no trace of iron for use as anode for an efficiency test to see if rotation would have the same effect here. It was thought possible that the voltage relation might be changed so that iron could be reduced and oxidized more easily than nickel deposited and dissolved, respectively, and therefore, that these reactions would go on more readily than the normal deposition of metal. The alternate oxidation and reduction of the iron, if this is the important factor, would be greatly increased by the rapid stirring and consequent mixing of the anode and cathode compartment occasioned by the rotating cathode. Attempts, however, to get a large amount of pure nickel were futile, more or less, so it was decided to change the plan.

If the cathode is enclosed in a porous cup, the iron will be almost wholly kept out, so that some factors would be changed with a probable change in the results. Consequently, two cells were run in series, one with, and the other without the porous cup. The solutions were iron-free, and contained, as all solutions henceforth, 8 grams of nickel ammonium sulphate and 1 gram nickel chloride per 100 cc of water. The chloride was added to aid the solution of the anodes (0.14 percent iron) which were used in several runs. The anodes used here, however, contained 7.6 percent iron. The current was as before. The deposits were weighed every fifteen minutes for one hour and at longer intervals after that, giving the time-efficiency curves shown in Fig. 2. The efficiency in the ordinary cell increases continuously, while that of the porous cup cell increases, reaches a maximum, and then falls off. Inside of the porous cup, the cathode compartment, after 15 hours' run, the solution consisted essentially of a rather concentrated solution of ammonium hydroxide, the nickel being almost wholly removed from the compartment by deposition. The cathode in the ordinary cell contained about 3.5 percent iron, the one in the porous cup containing only 0.15 percent. After the run the solution in the ordinary cell, 400 cc, had 0.4 gram of iron present. In the porous cup cell, 1.6 grams of iron were found inside the cup and 2.1 grams outside. The iron had practically all been precipitated by the ammonium hydroxide inside the porous cup. It was deposited before it reached the cathode and hence the iron content of the cathode in the cup was low.

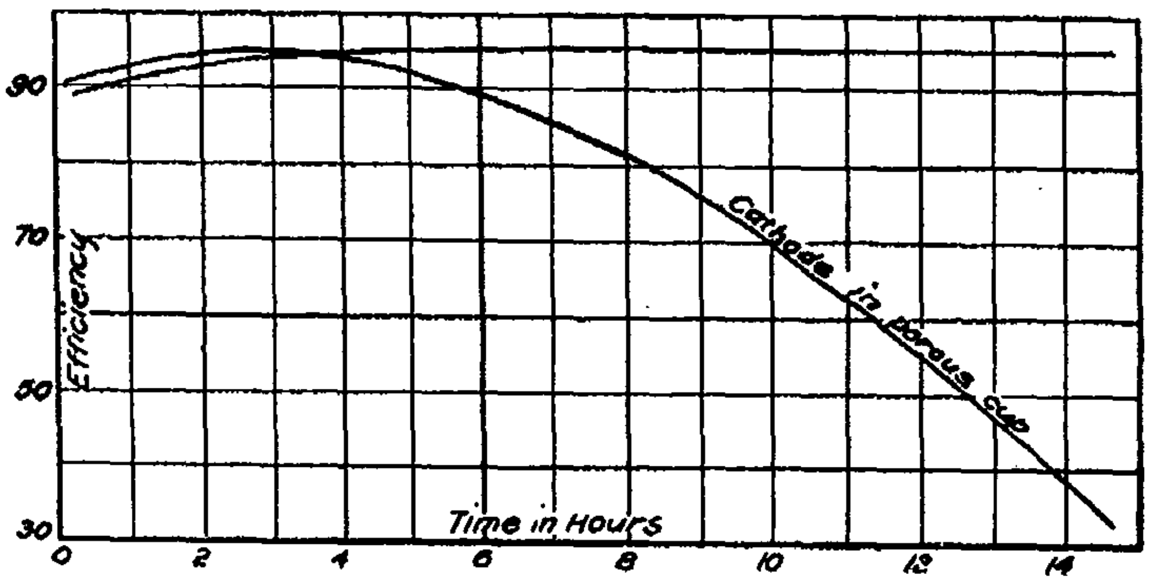

Fig. 2

The fact that the cathode compartment becomes alkaline leads one at once to an important consideration which probably throws light on the deposition of several of the metals more electropositive than hydrogen. If the measurement of the voltage required to deposit nickel,[1] 0.228 volt, and the measurement of the overvoltage of hydrogen[2] at the surface of a nickel cathode, 0.14 to 0.21 volt, mean anything, the fact that nickel is deposited instead of hydrogen from a solution giving a slight acid reaction, cannot be ascribed to the overvoltage of hydrogen, for the balance is in the other direc-

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[1] Wilsmore: Zeit. phys. Chem., 35, 318 (1900).

[2] Coehn: Zeit. phys. Chem., 38, 618 (1901); Caspari: Ibid., 30, 93 (1899).

tion. It is not going too far, probably, to say that hydrogen is liberated at a nickel electrode with a smaller expenditure of energy, than that required to deposit nickel. This leads directly, then, to the obvious conclusion that nickel cannot be deposited from an acid solution. When, however, the solution becomes slightly alkaline the nickel may be deposited, for the concentration of hydrogen as ion becomes practically zero in the alkaline solution. In interpreting this statement, it must be borne in mind that the acidity of the solution from which the actual deposition takes place is considered, and not that of the solution out between the two electrodes. The reference is, therefore, to the film of solution which is in actual contact with the cathode.

Under this condition, suppose an electrolysis is begun with nickel ammonium sulphate solution with nickel electrodes. The solution being neutral or slightly acid will contain the following positive ions,

$$H^{\cdot}, Ni^{\cdot\cdot} \text{ and } NH_4^{\cdot}.$$

These ions will all take part in carrying the current to the cathode. At the cathode hydrogen will be liberated, which removal leaves an excess of hydroxyl ions which with the $NH_4^{\cdot}$ ions corresponds to the ammonium hydroxide which accumulates at the cathode. No deposition of nickel can take place until the hydrogen is removed and the solution becomes alkaline. When this occurs nickel may deposit, and the efficiency of deposition will depend on the maintenance of a cathode film which is alkaline. The facts exhibited in the curves, Fig. 1, are intelligible from this viewpoint. When the electrolysis is started, the efficiency is low at first, due to the fact that much of the current is used up in liberating hydrogen. When these ions are removed, the cathode film is alkaline, and nickel deposits with an efficiency which gradually increases as the electrolysis proceeds, until practically a maximum value is reached, when the cathode film of solution is most favorable for the production of the best deposit.

The tendency to deposit hydrogen is greater at a platinum cathode than at a nickel cathode, on account of the over-voltage effect. It might be said, therefore, that with a platinum cathode, a low efficiency would be expected, since the tendency to liberate hydrogen is greater than when a nickel cathode is used. In the former case, some time is required to build up a surface of nickel, while in the case of a nickel cathode, the nickel film is present from the beginning. Having the nickel surface from the beginning, the over-voltage effect would operate over a longer time than in the case of a platinum cathode, and the tendency to deposit hydrogen would be less in the case of a nickel cathode. If the above were true, the efficiency would be lower with platinum than with copper or nickel cathodes. When these were tried practically no difference could be shown to exist, as is shown in Table I. The cells were run in series for 17 minutes.

TABLE I

Effect of cathodes on efficiency of deposition

Cathode material	Copper	Nickel	Platinum
Efficiency percent	95.5	96.0	95.3

These differences are well within the limit of experimental error and show that the cathode over-voltage has nothing to do with the efficiency.

If the increase in efficiency with time is due to the accumulation of ammonium hydroxide at the cathode, this condition could be realized synthetically throughout the whole solution, by adding to the solution some ammonium hydroxide. It ought to be possible to start the electrolysis with a high efficiency by adding the alkali to neutralize the acid present. Runs were therefore made with solutions (190 cc each) to which 2, 5, and 10 cc of 1 : 10 ammonium hydroxide (sp. gr. 0.89) were added. With 2 cc of material as is shown in Fig. 3, the efficiency is increased slightly over the neutral solution, the amount of increase being very great in the cases with 5 and 10 cc. The solution containing 5 cc of ammonium hydroxide always gave a more adherent and a better deposit. These runs are with stationary electrodes, the anodes being 0.5 percent iron, the cathode being copper, held stationary. The current density was about 1.5 amperes per square decimeter, and the cells were run in series with a coulometer as in other cases. It seems that the efficiency can be begun and maintained at almost any desired point within limits by adding ammonium hydroxide. The same effect is obtained with anodes containing 7.5 percent iron as is shown in Fig. 4. It is interesting to note the fact that iron is found in the cells after electrolysis as shown in Table II.

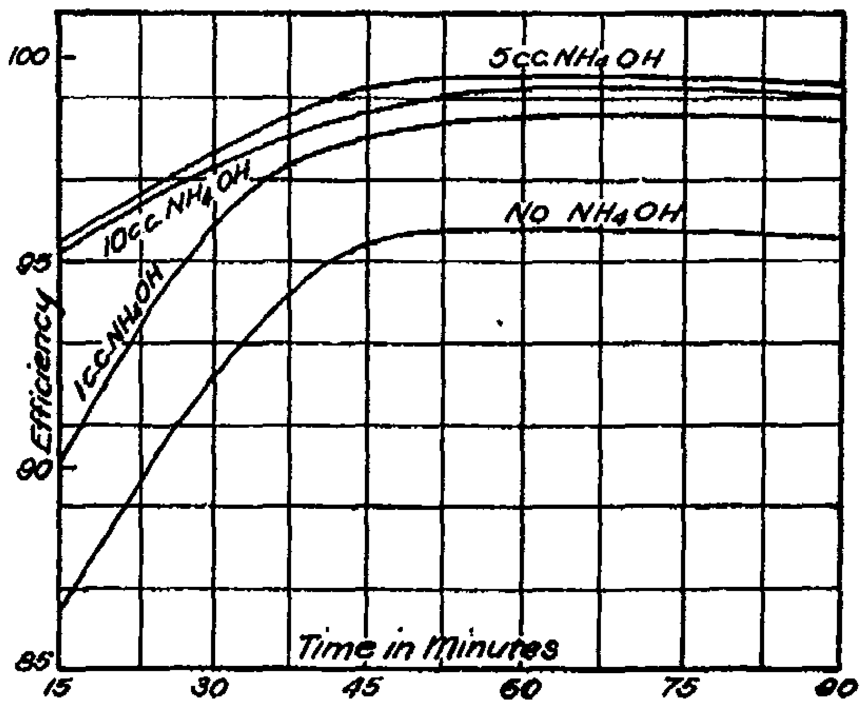

Fig. 3

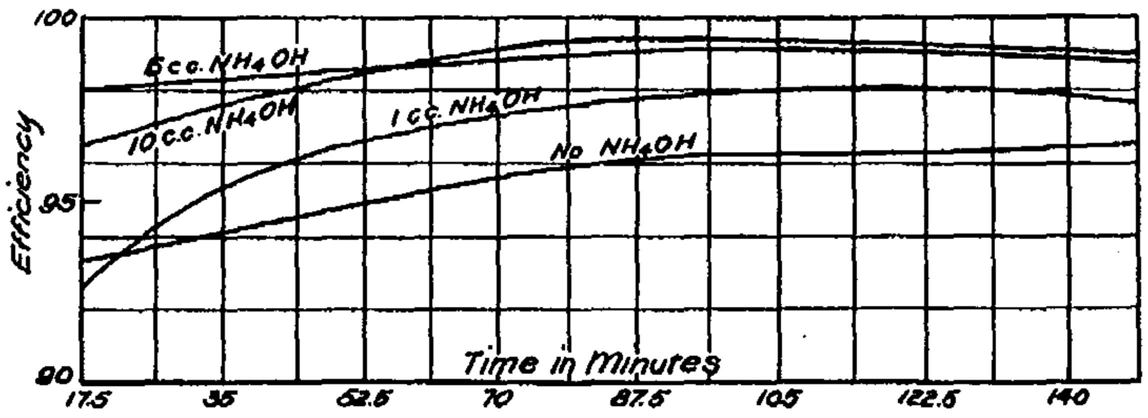

Fig. 4

TABLE II

Iron in cells with ammonium hydroxide

Amt. of ammonia cc	None	2	5	10
Iron in deposit at bottom of beaker, grams	0.0225	0.0300	0.0685	0.0442
Iron in solution, grams	0.0144	0.0092	Trace	Nil

The amount of iron in the precipitate on the bottom of the beaker increases as the concentration of alkali increases, while the amount in the solution decreases just as it should.

The explanation of the decrease in efficiency with the rotating cathode over the stationary one, becomes apparent at once. The rotation of the cathode stirs the solution and gives a very effective means of breaking up this alkaline film over the rotating part. This broken up, the efficiency is low by amounts depending on the efficiency of the removal of the ammonium hydroxide from the film. The stirring may just as well be considered as preventing impoverishment of hydrogen which of course amounts to the same thing, *viz.*, prevents the formation of an alkaline film over the cathode. The efficiency should begin lower than the stationary one and should increase as the electrolysis proceeds, since some ammonium hydroxide is piling up in the solution.

The efficiency of removal of a surface film will depend on the speed of rotation. It may be seen, therefore, that the efficiency should decrease as the speed of rotation is increased.

Although the method of removal of this film by stirring the solution is an inefficient one, it ought to be possible to decrease the efficiency by stirring the solution without rotating the cathode. This is a necessary conclusion from the theory given above. On the other hand, Calhane and Gammage have shown that when a stirrer is rotated 130 revolutions per minute the efficiency is not greatly different from the stationary one. They have carefully avoided stirring more vigorously even though it might easily be guessed that stirring vigorously out in the center of the solution would probably disturb the cathode film only as much as that occasioned when the cathode itself is revolved very slowly. It seemed safe to say, therefore, that if the stirring were more vigorous, the efficiency would be decreased. At any rate, since the theory requires this, the experiment had to be made. The results for two rates of stirring will be shown. The conditions were practically the same as before: nickel anodes, 0.14 percent iron, perforated platinum sheet cathodes, solution as before (80 grams nickel ammonium sulphate, and 10 grams nickel chloride per liter). The current density was about 1.5 ampères per square decimeter and the cathodes were weighed every 15 minutes. No coulometer was used, it being desired to see the difference between a stationary solution and one which was well stirred. The containers were crystallizing dishes 12.5 cm in diameter, the anode being placed on one side and the cathode on the opposite side. Situated about 2 cm from the cathode in one cell, was a cylindrical, perforated, sheet, platinum electrode about 3 cm in diameter and 5 cm long, fastened to a shank or shaft, which was held in a chuck and rotated. This gave very good stirring at the surface of the cathode sheet. The rotating piece, of course,

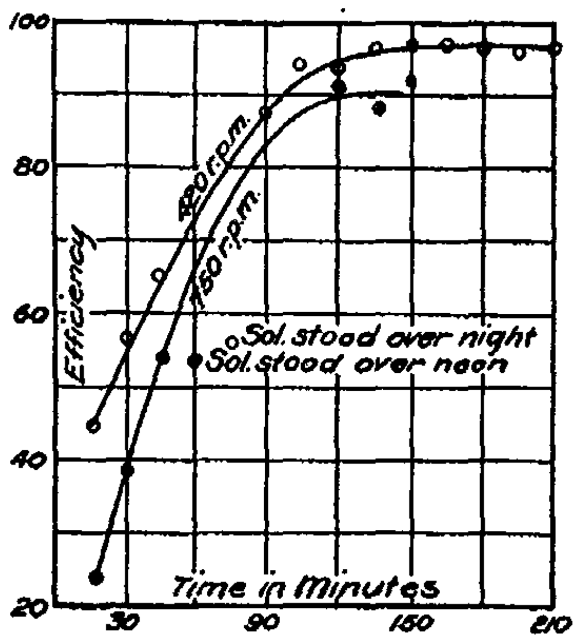

Fig. 5

was not electrically connected, it being used only for stirring. One run was made with stirrer rotated at 420, and another at 750 revolutions per minute. The former rate of stirring gives curve A, and the latter one, curve B, Fig. 5. These curves show relative efficiencies of the cells with a still solution and that with a stirred solution. In other words, they give the efficiencies of the stirred solution as compared with the still solution which is assumed one hundred percent. From these curves the conclusion may be drawn that the efficiency of deposition decreases, as the rate of stirring is increased, as it should according to the theory just advanced.

With this, a number of facts become intelligible which otherwise are weird. The curve at the top of Fig. 1, which was run at a higher current density than the other stationary curve, shows a higher efficiency because the rate of carrying in the ammonium ion is relatively greater as compared with its diffusion backward, the current density being higher. This gives conditions for the formation of a more alkaline film where the current density is higher, and therefore the higher efficiency.

As to the behavior of iron, it may be said that if it is deposited at a lower voltage than nickel,[1] it will be deposited first if it can get to the cathode. Where an ammoniacal film exists over the cathode the iron cannot get in, since it is deposited as hydrated oxide. But when the film is broken by rotation, iron may enter and be deposited. In other words, just as was found, the amount of iron in the deposit is greater with a rotating than with a stationary electrode. If iron is deposited after nickel,[2] it would be deposited when nickel is impoverished. When the electrode is rotated, this impoverishment is prevented. The increase of the iron content with increasing rotation would seem to indicate that Küster's conclusion is due to some specific effect other than the voltage relations. On the other hand, it was noted that the solution

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[1] Toepffer: Zeit. Elektrochemie, **6**, 342 (1899).

[2] Küster: Ibid., **7**, 690 (1901).

became clouded in the cell with a rotating electrode. It is possible, therefore, that some of the increase could be due to mechanical deposition of the hydrated oxide which presumably causes the clouding effect.

The best deposits are obtained when the solution is alkaline at the surface of the cathode. This would mean that at the time the best deposit of nickel is being obtained, it should be impossible to get iron deposited at the cathode unless it be by mechanical occlusion or deposition.

When the solution, which has been electrolyzed, has stood, the ammonium hydroxide necessary for good efficiency will diffuse away from the electrode and the efficiency will be less after standing, less than that obtained if the solution were worked continuously. This is shown very well in Fig. 5 where the solutions stood as noted, and it is seen from the curve that the efficiencies are very much lower than if run continuously. From the measurements as taken from the work of Calhane and Gammage, 12 percent efficiency was obtained with a rotation of 130 R. P. M. Then with 260 R. P. M., 69 percent was obtained. It appears that both must have been made in the same solution. If so, it is unfortunate that they did not try to duplicate the 130 R. P. M. run in the same solution after running the 260 R. P. M. one. The efficiency would probably have been about 70 percent instead of 12 percent.

It may be concluded that:

A good deposit of nickel may be obtained from the double sulphate if the solution at the surface of the cathode is kept alkaline.

The efficiency is dependent upon the degree of alkalinity of the cathode film.

The efficiency can be started high and maintained high by adding a definite amount of ammonium hydroxide to the solution.

The alkaline solution film at the cathode may be disturbed and the efficiency of deposition decreased, by stirring the solution vigorously.

Since alkalinity is necessary for good efficiency, it is very probable that in acid solutions, nickel is deposited only when impoverishment of the hydrogen ions has caused the solution to become alkaline and given the conditions where nickel may deposit.

The iron content of a deposit formed on a rotating cathode, is greater than that formed on a stationary electrode. This may be due to mechanical occlusions.

The iron content of the anode does not materially affect the efficiency.

Electrochemical Laboratory
Cornell University

THE THEORY OF DYEING. III

BY WILDER D. BANCROFT

Since dyeing is in general a case of selective adsorption by the fiber, we should expect to find all degrees of adsorption. If the amount of adsorption is low and if the fiber consequently shows no tendency to exhaust the bath, the dye in the fiber will wash out readily and the practical dyer will say that that dye does not dye that fiber. For practical reasons the dyer does not recognize the innumerable gradations of adsorption which actually occur with different dyes and different fibers. To him a dye either dyes or does not dye a given fiber. Thus, methylene blue is not supposed to dye cotton; but one has nevertheless to wash cotton thoroughly to remove all the methylene blue. The distinction is a good one practically; but it should not be allowed to interfere with the theoretical treatment of the subject. We are actually dealing with differences in degree, not differences in kind.

There are some dyes which are not adsorbed strongly by wool and very many which are not adsorbed strongly by cotton. Satisfactory results can be obtained only by use of mordants,[1] which are "substances by means of which we are able to fix coloring matters, which of themselves have [little or] no affinity for the fabric." The term and conception date back a good way. Thus my name-sake[2] says: "Adjective coloring matters are generally soluble, in a great degree at least, by water; though some of them derive their solubility from an intermixture of what has been called *extractive* matter; which being separated in the dyeing process, after the adjective color has been applied to the dyed substance, their union becomes thereby more intimate and permanent. But in other respects, adjective colors owe their durability, as well as their lustre, to the interposition of some

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[1] Crace-Calvert: "Dyeing and Calico Printing," 17 (1878).

[2] Bancroft: "Philosophy of Permanent Colors," 1, 341 (1813).

earthy or metallic basis; which, having a considerable attraction, both for the coloring matter and the stuff to be dyed, serves as a bond of union between them, and obviates that disposition to suffer decomposition and decay, which naturally belongs to such coloring matters when *uncombined*. These earthy and metallic bases, having been commonly employed in a state of solution or combinations with acids, were from that circumstance denominated *mordants* (biters or corroders) by the French, who, indeed, began to employ the term long before a theory of dyeing had been conceived; whilst even alum was supposed to act by its sulphuric acid, and not by the pure clay upon which its usefulness depends, and whilst in truth all the other matters called mordants were supposed to be useful only by their solvent or corroding powers; and the term, having been thus employed, has since been adopted in other countries. The ingenious Mr. Henry, of Manchester, has, however, lately objected to it with great reason, and has proposed in its stead to employ the term *basis*, which seems defective only, inasmuch as it does not express the particular *affinity* or *power of attraction*, manifestly subsisting between these earthy and metallic substances, and the several adjective coloring matters, as well as between the former and the fibers of wool, silk, cotton, etc. I confess, however, that no other more suitable term has occurred to me; and being unwilling to propose new terms, without some cogent reason, I shall sometimes employ that of mordant as well as that of basis; though not indiscriminately in all cases; since I shall generally use the former to signify earthy and metallic substances when *actually dissolved* by some acid, alkaline, or other solvent, and when, of course, they will commonly prove more or less corroding or biting, according to the original meaning of the term. But the denomination of basis will be most frequently used to designate the same earthy and metallic substances, distinctly and separately from any acid or other solvent, when actually fixed in the pores of fibers of wool, silk, etc., or when it is not intended to notice any property in them, which may more immediately result from their combinations with any particular menstruum. M. Berthollet, indeed, gives the term mordant a much more extensive signification, as meaning all the different chemical agents capable of serving as *intermedia* between the several coloring particles and the stuffs so dyed with them, either for the purpose of assisting their union or of modifying it. This last effect (of modification) may, however, be produced by a variety of matters besides those which are of the earthy or metallic kinds, and indeed by everything capable, not of fixing, but of merely varying the shades of adjective coloring matters. These, therefore, I think it more proper to designate, not as mordants or bases, but as *alterants*, whose use and application may in this respect be extended to substantive as well as to adjective colors."

A mordant can be defined as a substance which is adsorbed strongly by the fiber and which adsorbs the color strongly. When dyeing mordanted cloth, we really dye the mordant in most cases rather than the fiber itself. When the mordant is dyed with no fiber present, the dyed product is called a lake, though the lakes used as pigments are usually thrown down on, or together with, barium sulphate, china clay, lead sulphate, red lead, or some other suitable medium intended to modify the physical properties. For acid dyes the usual mordants are the hydrous oxides of aluminum, chromium, iron, tin, copper, lead, etc., while the basic dyes are mordanted with tannin, fatty acids, albumin, silicic acid, arsenic acid, or phosphoric acid. The basic dyes are also sometimes mordanted with the direct cotton colors.[1] Sulphur and other substances may be used as mordants in special cases. A satisfactory theory of dyeing must account for the action of the specific mordants, and also for the action of the so-called fixing agents. The metallic mordants can be fixed, or made to hold faster to the fiber by treatment with silicates, arsenates, phosphates, tannin, or fatty acids, lime, magnesia, and the hydrous oxides of zinc, nickel, and cobalt are helpful in

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[1] Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 2nd Ed., 378 (1910).

conjunction with other fixing agents. Lime seems to be essential when alumina is used as a mordant for alizarine; but it is quite possible that the lime helps fix the color to the mordant rather than the mordant to the fiber. The acid mordants can be fixed by metallic mordants in general, while tartar emetic is the best fixing agent for tannin. The theory of mordants, therefore, involves four different things: the relation between the fiber and the mordant, the relation between the mordant and the fixing agent, the relation between the mordant and the dye, and the relation between the dye and the fixing agent.

Most people consider: that the mordant forms a definite compound with the fiber in the case of wool, though not in the case of cotton; that the mordant forms a definite compound with the dye; that the mordant forms a definite compound with the fixing agent; and that the dye forms a compound with the compound formed by the interaction of mordant and fixing agent. Knecht, Rawson and Loewenthal[1] say: "The name [mordant] is derived from the French word *mordre* (to bite or corrode), because the early French dyers believe that the utility of the metallic salts they employed consisted in their corrosive nature; it was believed that these substances opened the pores of the textile fibers and thus rendered them capable of absorbing the dyestuffs. At a later period it was recognized that the so-called mordants entered into a chemical combination with the dyestuffs and formed insoluble compounds or 'color lakes;' hence these substances were considered principally as fixing agents for the dyestuffs. In many cases this is true—*i. e.*, where a dyestuff dyes without the aid of mordants, and becomes simply faster to washing and milling by the application of the mordant. In most cases, however, the mordant is an essential constituent of the color, as without it no color at all or only a worthless shade is produced. We consider as mordants substances which, partly or wholly, combine with the dyestuffs to form definite compounds

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[1] "A Manual of Dyeing," 2nd Ed., 4, 20, 179, 189, 224, 234 (1910).

in the fiber, thus distinguishing them from those compounds which take part in the dyeing process without entering into the composition of the ultimate color. . . .

"The mordants may be classified as *acid* and *basic* mordants. The acid mordants, of which the tannins and the oil (fatty acid compounds) mordants are the most important, serve for the fixation of basic dyestuffs and metallic oxides; they are often used for fixing basic mordants on the fiber, which latter then act as the true mordants in dyeing. Their chief application is in the dyeing of cotton and linen, and in silk weighting. The basic mordants contain the hydrated oxides of the heavy metals as their active constituents; of this class the most important are compounds (salts) of aluminum, iron, chromium, copper, and tin. In accordance with their basic character, these mordants serve for the fixation of acid or phenol-like dyestuffs.

"As far back as the eighteenth century it was observed that for the dyeing of cotton with madder and alumina mordants calcareous water was necessary; the influence of lime in water used for dyeing with other mordants and dyestuffs was also noticed. In 1882, Horace Koechlin, in a communication to the Société Industrielle de Mulhouse, pointed out that certain coloring matters could be more readily fixed on cotton by means of *double mordants,* (containing two metals) than by simple ones. Such double mordants were prepared by mixing aqueous solutions of acetate of alumina, or acetate of chrome with either acetate of lime or acetate of magnesia. He showed that calico prepared with such mordants could be dyed with Phloxin, Scarlet 3R, and other coloring matters. Some years later he recommended for the fixation of St. Denis red a treble mordant consisting of alumina, magnesia, and oxide of zinc, and showed that this treble mordant was also capable of fixing other azo dyes, yielding bright shades which were comparatively fast to soap.

"Following up this subject more closely from a scientific point of view, Prud'homme, taking as his starting point Vauquelin's observation that alumina precipitated in presence of magnesia is insoluble in caustic alkalies, discovered that, beside magnesia, other metals possess the property of producing compounds with alumina insoluble in alkalies, which are useful as mordants; and further, that other metallic oxides which are soluble in alkalies are capable of yielding, like alumina, insoluble compounds of this character of *compound mordants*. Nickel and cobalt salts, for instance, act better than magnesium salts in rendering the precipitated alumina insoluble in caustic soda, while tin and zinc salts form with each other a compound mordant which is also insoluble in caustic soda. Prud'homme maintains that in cotton dyeing compound mordants are invariably produced, either intentionally or accidentally on the fiber, and that there is no such thing as a simple mordant. The best mordants consist of compounds of sesquioxides, like alumina, chromic oxide, or ferric oxide, with monoxides, like lime, magnesia, or zinc oxide. In some cases treble mordants give even better results. Thus iron fixed with arseniate of soda or phosphate of soda gives better results with lime or magnesia than without these oxides."

"The *mordanting* of wool and silk appears to be analogous to the dyeing of these fibers, and to depend upon their acid and basic properties. Thus, wool boiled with a solution of aluminum sulphate fixes both the acid and the basic constituent of the salt; but, being possessed of more pronounced acid than basic properties, it absorbs the basic constituent more energetically than the acid one, and some free acid is left in the solution. By subsequent treatment with boiling water, more acid is extracted, and the alumina becomes more firmly combined with the substance of the fiber. It is noteworthy that only such salts which contain the acid and basic constituents in a comparatively loose state of combination are absorbed by the wool fiber. Thus, whereas the sulphates of aluminum, iron, chromium, and copper are readily taken up from the boiling solutions by the wool fiber, sodium sulphate or sodium chloride are not taken up at all. Chromic acid, on the other hand, is readily taken up by wool, and, like the acetates of the heavy metals, is precipitated from its aqueous solution by lanuginic acid."

"The application [of the tannin-substances] in dyeing is based on the fact that they are readily absorbed by the textile fibers, notably by cotton, linen, and silk; and on the property of forming insoluble compounds in the fibers, on the one hand with the heavy metals and with antimony, and on the other hand with the basic dyestuffs."

"Tannic acid forms lakes with the basic colors, which are insoluble in pure water, but dissolve in an excess of tannin and in other acids. The tannic acids can be converted into various metallic salts, which are insoluble in tannic acid or in water, and which, when produced in the fiber, resist soaping very well. These insoluble salts possess the same property as tannic acid in the free state of forming lakes with the basic colors; but an excess of the salts has no dissolving action on the color lakes, and the products are very stable. There are in this way produced in the fiber *triple compounds* of tannic acid, a metallic oxide and a basic color, which are quite insoluble in water, and resist both washing and soaping extremely well; and they are also faster to light than the lakes of tannin and coloring matter which do not contain a metallic oxide."

"Sodium phosphate precipitates from the solutions of aluminum salts *aluminum phosphate*, $AlPO_4$. $Al_2(SO_4)_3 + 2Na_2HPO_4 = 2AlPO_4 + Na_2SO_4 + 2NaHSO_4$. The precipitate forms a voluminous white mass, which is soluble in caustic soda, but not in ammonia. It also dissolves in hydrochloric or nitric acid, but not in acetic acid. Citric acid prevents the formation of the precipitate but not tartaric acid or sugar. Aluminum phosphate is soluble in the aqueous solutions of other aluminum salts. One equivalent of aluminum sulphate, $Al_2(SO_4)_3$, can keep one equivalent of aluminum phosphate, $AlPO_4$ in solution, according to Liechti and Suida. This is probably the reason why sodium phosphate is not a good fixing agent for aluminum mordants. Sodium arsenate precipitates from the solutions of aluminum salts *aluminum* *arsenate* as a white powder, which is insoluble in water, but soluble in acids. This reaction is used to fix aluminum mordants on the vegetable fibers. Sodium silicate precipitates from the solutions of aluminum salts aluminum hydroxide; the silicic acid does not combine under these conditions with alumina; if the silicate of soda contains an excess of caustic soda, the precipitate of aluminum hydroxide may redissolve in the precipitant."

"*The composition of the mordant which is retained by the fiber* varies with the different fixing processes. In almost every case aluminum hydroxide is formed either by mere dissociation of the aluminum salt, or by decomposition of the same with ammonia, or with sodium or ammonium carbonate, or with chalk, etc. In addition, arsenate and phosphate of soda generate more or less aluminum arsenate, and phosphate; soap produces stearate, palmitate, or oleate of aluminum; whereas silicate of soda forms the hydroxide only. If the material was prepared with tannic acid, oil or soap, tannate, etc., of aluminum is formed; the mordanting with stannate and alum produces only stannic hydrate and aluminum hydroxide. In case a basic sulphate is fixed exclusively by aging, very basic sulphates are formed, which, being insoluble in water, are retained, together with the hydroxide, while the neutral sulphate and free acid, which were formed by dissociation through aging, are removed by washing. It is, however, more usual to pass the goods after the aging through some fixing bath—*e. g.*, chalk or phosphate—which remove probably the whole amount of the sulphuric acid."

Parry and Coste[1] say: "The neutral color lakes may, in general, be regarded as compounds of one or more natural color acids with inorganic bases, with, at times, more or less mechanical admixture of excess of base or acid. Theoretically, however, the lake may be regarded as the true compound in the sense described. In the same way the lakes of the artificial color must be regarded as true chemical com-

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[1] "The Chemistry of Pigments," 240 (1902).

pounds, although the mechanical admixture plays an important part in the preparation of the colors in actual practice.

"For the purposes of the present chapter, artificial coloring matters capable of forming lakes may be divided into three groups. These are as follows: (1) The artificial color bases containing nitrogen in combination with hydrogen, so that the base behaves as an ammonia derivative. (2) Artificial colors of a purely acid nature, capable of combining with an inorganic base. (3) Artificial colors in which both acid and basic functions exist simultaneously in a well-defined degree. Such bodies may be typified by a sulpho acid of an amido compound.

"In this sense then we understand a true lake, and it is necessary to here draw attention to the somewhat free use of the word 'base' in connection with this subject. As we are employing the word, it refers to a compound or an oxide of a metal capable of uniting to form a definite compound with an acid. The word is also employed ('lake base,' etc.) when referring to a neutral body, such as sulphate of barium or china clay, which is employed as an absorbent, or as a diluent for a color, but in the present work the word will not be employed in that sense.

"At the same time it must be admitted that the principles of lake formation are not altogether as well understood as one could wish. Although we have emphasized the importance of recognizing the principle of true chemical combination as the basis for the formation of lakes, there is considerable room for speculation as to the degree to which this combination is carried in a great number of cases which must be regarded as belonging to the class of true lakes. It is quite certain that advantageous precipitation of color bases takes place, when only a small proportion of the calculated molecular equivalent of the precipitating acid is used. This is especially the case when tannic acid is employed. Here, then, we have a case in which, whilst there is certainly a true chemical combination of the base and the acid, there exists in the compound far more base than the theoretical combination would require.

It is usual to use the expression 'mechanical combination' in such cases, and to escape from the difficulty of a lame explanation by the use of a term which is even more difficult to define than the original problem is to explain. In certain cases, where a voluminous precipitate, such as that of alumina in the hydrated state, is thrown down, a species of 'mechanical combination' is not difficult to assume. For example, when one adds a solution of ammonia to a solution of alum mixed with a salt of calcium, a voluminous precipitate is thrown down. It is of such a bulky, gelatinous nature that together with the mass of water which assists to make up the 'jelly,' there is a considerable amount of lime salts; it is next to impossible to completely remove these lime salts by ordinary washing with water, and when the alumina is filtered off and dried, it will be found that there still remains an appreciable amount of lime in a state of intimate admixture with the alumina. But the quantity is not sufficient to explain the almost complete precipitation of a considerable excess of base by a small quantity of the precipitating acid, as in the case we have quoted.

"From a prolonged experience of compounds of the inorganic elements, which are more easily manipulated than the organic compounds from this point of view, we are acquainted with well-defined basic compounds, *i. e.*, compounds of a base with an acid which are not of normal constitution, but contain definite molecular proportions of the base in excess of that required for the normal compound. In our present imperfect state of knowledge concerning the exact nature of the combination existing between many organic compounds, it appears to us that the most feasible explanation of the somewhat erratic combinations of these lake bodies is the existence of an analogous series of compounds to those which, as just mentioned, are well recognized between inorganic elements. This, however, is merely a matter of speculation, and need not, therefore, be further discussed here. We now pass on to the consideration of the coal-tar lakes, and in doing this we have arranged the lakes in groups according to their colors, without taking their chemical constitution into consideration, a practice which, as evident in the earlier chapters, would not have been convenient when dealing with the pigments of inorganic origin."

Friend[1] also considers that lakes are or should be definite compounds. "Most natural coloring matters are acidic in character, and can, therefore, combine with basic bodies, such as the oxides and hydroxides of metals. The products thus obtained are colored, and insoluble in water; they, therefore, possess two of the qualities necessary to render them serviceable as pigments. Theoretically, the amount of basic substance should be exactly sufficient to neutralize all the acid color—neither more nor less—to form a true lake. Practically, however, this rule is not adhered to, an excess of base being usually employed in such quantities as to produce the desired shade. The greater the proportion of the base, the lighter will be the tint, for obvious reasons. As the color and metallic base have such a strong affinity for one another, it is generally sufficient to mix solutions of the two, when the lake separates out. Sometimes, however, the addition of small quantities of sodium carbonate is necessary to effect the precipitation."

Knecht and Hummel[2] do not even discuss the possibility of the fixing agents not forming definite compounds with the mordants. "Silk may be often mordanted in the same manner as wool, but as a rule it is treated like cotton. The silk is steeped for several hours in cold, neutral, or basic solutions of chromium chloride, alum, ferric sulphate, etc., then rinsed in water slightly, and passed into a cold dilute solution of silicate of soda, in order to fix the mordants on the fiber as insoluble silicates. Cotton does not, like wool and silk, possess the property of decomposing metallic salts, hence the methods of mordanting this fiber are more complex, and vary according to the metallic salts and coloring matters employed,

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[1] "An Introduction to the Chemistry of Paints," 101 (1910).

[2] "Encyclopedia Britannica," 11th Ed., 8, 748 (1910).

as well as the particular effects to be obtained. One method is to impregnate the cotton with a solution of so-called 'sulphated oil' or 'Turkey red oil;' the oil-prepared material is then dried and passed into a cold solution of some metallic salt—*e. g.*, aluminum acetate, basic chromium chloride, etc. The mordant is thus fixed on the fiber as a metallic oleate, and after a passage through water containing a little chalk or silicate of soda to remove acidity, and a final rinsing, the cotton is ready for dyeing. Another method of mordanting copper is to fix the metallic salt on the fiber as a tannate instead of an oleate. This is effected by first steeping the cotton in a cold solution of tannic acid or in a cold decoction of some tannin matter, *e. g.*, sumach, in which operation the cotton attracts a considerable amount of tannic acid; after squeezing, the material is steeped for an hour or more in a solution of the metallic salt and finally washed. The mordants employed in this case are various—*e. g.*, basic aluminum or ferric sulphate, basic chromic chloride, stannic chloride (cotton spirits), etc. There are other methods of mordanting cotton besides those mentioned, but the main object in all cases is to fix an insoluble metallic compound on the fiber. It is interesting to note that whether the metallic oxide is united with the substance of the fiber, as in the case of wool and silk, or precipitated as a tannate, oleate, silicate, etc., as in the case of cotton or silk, it still has the power of combining with the coloring matter in the dyebath to form the colored lake or dye on the material."

I propose to show that no definite compounds are formed as a rule when dyeing with mordant colors. The fiber adsorbs the mordant, the mordant adsorbs the dye, and the mordant adsorbs the fixing agent. It is not impossible that definite compounds are formed with special substances or under special conditions; but I claim that these are merely unimportant cases and that they have no significance for the general theory of dyeing.

The taking up of mordants by wool is like the case of the adsorption of alkali or acid, with the exception that the adsorbed bases are practically insoluble in water and consequently do not tend to wash out in water to any appreciable extent. It is perhaps desirable to give some data, in support of this, though it must be admitted that the experiments have never been done in the proper way. Pelet-Jolivet[1] gives figures for wool with aluminum chloride, potassium bichromate, potassium chromate, and chrome alum, Table I.

TABLE I

3 g wool, 200 cc solution		5 g wool, 200 cc solution	
Aluminum chloride		Potassium bichromate	
Grams in solution	Grams adsorbed	Grams in solution	Grams adsorbed
0.007	0.0037	0.0976	0.0024
0.0038	0.0183	0.1902	0.0098
0.0304	0.0138	0.2324	0.1676
0.1256	0.0956	0.304	0.206
0.8596	0.0252	1.101	0.299
2.1465	0.655	—	—
3.832	0.392	—	—
5 g wool, 200 cc solution		5 g wool, 200 cc solution	
Potassium chromate		Chrome alum	
Grams in solution	Grams adsorbed	Grams in solution	Grams adsorbed
0.1887	0.0113	0.1818	0.0182
0.5861	0.0139	0.5831	0.0169
0.9807	0.0193	0.9766	0.0234
1.3749	0.0251	1.159	0.241
—	—	1.743	0.257

One difficulty with these data is that they do not really represent the facts. In the case of aluminum chloride, a certain amount of this substance purports to have been adsorbed. Though it is not so stated, it is certain that the author determined the amount of alumina adsorbed and then cal-

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[1] "Die Theorie des Färbeprozesses," 78, 79 (1910).

culated this into aluminum chloride. It is quite impossible that the aluminum chloride could have been adsorbed without decomposition. The irregularity of this series is in itself a proof of disturbing factors. A similar criticism applies to the other cases in Table I. In spite of these defects, it is quite clear that there is no evidence for the existence of two solid phases, and that, consequently, the taking up of alumina and of hydrous chromium oxide by wool is a case of adsorption.

An independent way to check this conclusion is to postulate the adsorption and then to see to what extent this enables us to account for and to criticize the results obtained by other people. Aluminum salts hydrolyze to a certain extent cold and to a greater extent when the solution is heated. The hydrous oxide set free may remain apparently dissolved but really as a colloidal suspension; or it may coagulate and precipitate, depending on the conditions of the experiment. Other things being equal, the tendency of the alumina to coagulate will be greater the higher the concentration of the hydrous alumina. Excess of acid will force back the hydrolysis and the hydrolysis will be less the stronger the acid that is used. Since the fiber adsorbs hydrous alumina, by hypothesis, the hydrolysis will proceed farther in presence of the fiber than when no fiber is present. While it is true that the hydrolysis will proceed farther the less acid the solution, it does not follow that the ideal condition for mordanting is a neutral or alkaline solution. We must consider also the rate of hydrolysis because it is essential for the fiber to hold the hydrous oxide as well as to set it free. Consequently it may be beneficial to have in the solution substances which retard the precipitation or coagulation of the hydrous oxide. From a neutral or basic aluminum sulphate solution, the alumina might easily precipitate in relatively large masses which would be chiefly on the surface of the fiber and which would not be held fast by it. Adding organic acids might very well retard coagulation sufficiently to enable the alumina to be taken up in a more satisfactory form of the fiber. If one impregnates the fiber with a solution of aluminum acetate and then steams the fiber, the acetate will be driven off gradually, and hydrous alumina will be set free slowly, thus permitting of a very effective adsorption. Since the object of getting the mordant into the fiber is to have something there which will adsorb the coloring matter, the ideal thing would be to precipitate the alumina in the form in which it would hold fastest to the cloth, would have the maximum transparency, and would adsorb the greatest amount of dye. It is not probable that the mordant can be obtained in such a form that it would satisfy all these requirements to the highest degree simultaneously. We shall, therefore, expect to find that the properties of the mordant vary with the treatment and that one strikes a balance so as to get the mordant in the form which is most generally useful.

Liechti and Suida[1] have done some work on the behavior of the solutions of some salts of alumina and iron. "The operation of mordanting textile fibers with aluminum, iron, and chromium salts consists in presenting solutions of these in such a condition to the fiber, that it shall be readily and completely impregnated with them, so that under the influence of the fiber itself and by certain physico-chemical processes the oxides or very basic salts are precipitated thereupon. The insoluble metallic compounds thus deposited in, on, or among the fibers form the mordant in its narrowest sense, combining, as they do, with the coloring matters either chemically or mechanically, thus rendering it possible to dye the fiber. Alizarine, for example, is a yellow-colored body which alone does not dye, but which can combine chemically with the oxides of aluminum, iron, and chromium, to form the actual colors—red, pink, black, violet, and reddish brown. The authors' task has been to study what influences the various acids, combined with the sesquioxides (R_2O_3) of iron, aluminum, etc., would have upon the behavior of the salt solutions with respect to the fiber to be mordanted. This necessitated the study of the dissociation of various normal and basic solutions,

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[1] Jour. Soc. Chem. Ind., 2, 537 (1883).

and also their behavior towards the fibers under conditions similar to those which obtain in the practical operations of the dyeing and printing. The present paper deals only with the phenomena of dissociation of various alumina and iron salts, in which the amount of alumina or ferric oxide was exactly the same. Soluble basic salts were prepared from concentrated solutions of the normal salts by adding to the latter various amounts of sodium carbonate, sodium bicarbonate, or the corresponding hydrated oxide. There was also prepared a number of normal and basic salt solutions in which the base is apparently in combination with only two molecules of acid radicals, because such salts play an important part in practice. In determining the dissociation point by heating, equal volumes of the solutions were put into test-tubes of equal diameter, and these were partially immersed in a large glass beaker filled with water, and containing a thermometer. The water was heated very gradually to the boiling point, and the dissociation point was determined from this thermometer, an experiment having shown that it registered exactly 1° lower than if placed in the solution in the test-tube. The dissociated mordant solutions were allowed to cool in order to see if the precipitate would redissolve or not. In determining the dissociation point by dilution, equal volumes of the mordants were mixed with gradually increasing amounts of water, and the mixtures were allowed to stand for five minutes. In this way the exact amount of solution was ascertained which was just necessary to cause turbidity or the beginning of dissociation. To determine the amount of water necessary to precipitate the alumina completely the separate liquids were filtered and the amount of alumina in the filtrate was estimated. In these experiments of dilution a natural water containing 0.0748 g. CaO and 0.0114 g. MgO per liter was taken, in order to give a practical bearing to them. In all cases the dilution was limited to such an amount that the CaO and MgO of the water could have no appreciable action. With respect to the behavior of the various aluminum mordants, no decomposition took place with any of the normal salts, either in boiling or diluting. With an increase in their basic condition the sulphates and acetates, and in a less degree the sulphocyanates, showed an increasing liability to decomposition by heating, while the basic chlorides were not dissociated either by boiling or by dilution, even when four molecules of acid radicals were withdrawn. By dilution with water there were decomposed only the basic sulphates, sulphoacetates and those basic acetates which contained in solution a sulphate, *e. g.*, Na_2SO_4; whereas, acetates (even when basic), free from H_2SO_4, also chlorides, nitrates, and sulphocyanates, could be diluted with water at the ordinary temperature without undergoing decomposition. Since it appeared to be of practical importance to gain some definite information as to the behavior of the mordants to the fiber, and the amount of mordant fixed on the latter during such operations as are actually adopted in practice, experiments were made with the most usual mordants in the following manner: A weighted quantity of cotton was evenly impregnated with, say, an alum mordant until its weight was exactly doubled, and then hung in a dry place on glass rods for 36 hours. A certain portion was then incinerated in order to determine the amount of alumina which the fiber had at its command. Another portion of the prepared fiber was then dried in a constant air current for six hours at a temperature of 40° C. The fiber was then washed for six hours with a definite amount of distilled water, and the amount of alumina in it was carefully estimated. From the number obtained it was possible to determine the percentage of alumina which had become fixed on the fiber.

"*Aluminum Sulphates.*—Crystalline aluminum sulphate from the Baden Aniline and Soda Works in Ludwigshafen, and also a melted commercial sulphate, were used in order to prepare other alumina mordants. These commercial salts had as nearly as possible the composition $Al_2(SO_4)_3.18H_2O$. Basic aluminum sulphates were prepared by partially neutralizing a solution of the above with carbonate of soda crystals, Solvay soda, or sodium bicarbonate, or by dissolving aluminum hydrate in normal aluminum sulphate. The strength of the solutions corresponded either to 200g or 150g normal sulphate per liter. The following mordants, among others, were prepared:

(1) $Al_2(SO_4)_3$. 200g normal aluminum sulphate dissolved in one liter H_2O.

(2) $Al_2(SO_4)_2(OH)_2$. 200g normal sulphate + 31.82g Na_2CO_3 per liter, according to the equation:

$$Al_2(SO_4)_3.18H_2O + Na_2CO_3 + H_2O = Al_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2 + 18H_2O$$

(3) $Al_2(SO_4)_2(OH)$ as No. 2, but only 150g normal sulphate per liter.

(4) $Al_4(SO_4)_3(OH)_6$. 200g normal sulphate and 75.7g sodium bicarbonate per liter, according to the equation:

$$2Al_2(SO_4)_3.18H_2O + 6NaHCO_3 = Al_4(SO_4)_3(OH)_6 + 3Na_2SO_4 + 3CO_2 + 36H_2O$$

(5) $Al_2(SO_4)(OH)_4$. 300g normal sulphate and 151.3g $NaHCO_3$ according to the following equation:

$$Al_2(SO_4)_3.18H_2O + 4NaHCO_3 = Al_2SO_4(OH)_4 + 2Na_2SO_4 + 4CO_2 + 18H_2O$$

TABLE A

Formula	Dissociation on heating			Dissociation on dilution	
	Start	At 100°	On cooling	Start	End
1. $Al_2(SO_4)_3$	—	—	—	—	—
2. $Al_2(SO_4)_2(OH)_2$	—	—	—	14 vols.	30 vols.
3. $Al_2(SO_4)_2(OH)_2$	—	—	—	10 vols.	22 vols.
4. $Al_4(SO_4)_3(OH)_6$	68°	Jelly	Ppt. remains	2 vols.	25 vols.
5. $Al_2(SO_4)(OH)_4$	Keeps only a short time			1/2 vol.	—

Formula	Attraction of the fiber during mordanting and drying		
	Al_2O_3 presented to the fiber, grams	Al_2O_3 fixed by the fiber grams	Percentage
1. $Al_2(SO_4)_3$	0.6971	0.0901	12.92
2. $Al_2(SO_4)_2(OH)_2$	0.4473	0.2283	51.04
4. $Al_4(SO_4)_3(OH)_6$	0.1527	0.0897	58.74

From Table A it will be seen that the more basic the mordant the more readily is it dissociated either on heating or on diluting with water, and the greater is the proportion of alumina fixed on the fiber by steeping, hanging, and drying. Other experiments showed that the dissociation was accelerated by the presence of Na_2SO_4 in the mordant solution.

"*Aluminum Sulpho-acetates.*—These mordants were prepared either by double decomposition of the normal aluminum sulphate with lead acetate or by adding acetic acid to solutions of basic sulphates. The following mordants among others were prepared:

(1) $Al_2(SO_4)(CH_3CO_2)_4$. 200g normal sulphate and 227.6g lead acetate per liter according to the equation:

$$Al_2(SO_4)_3.18H_2O + 2Pb(CH_3CO_2)_2.3H_2O = Al_2(SO_4)(CH_3CO_2)_4 + 2PbSO_4 + 24H_2O$$

(2) $Al_2(SO_4)(CH_3CO_2)_3(OH)$. 200g normal sulphate, 25.2g sodium bicarbonate and 170.6g lead acetate per liter, according to the equation:

$$2Al_2(SO_4)_3.18H_2O + 2NaHCO_3 + 3Pb(CH_3CO_2)_2.3H_2O = 2Al_2(SO_4)(CH_3CO_2)_3(OH) + 3PbSO_4 + Na_2SO_4 + 45H_2O$$

(3) $Al_2(SO_4)(CH_3CO_2)_2(OH)_2$. 200g normal sulphate, 31.8g Na_2CO_3 and 113.8g lead acetate, per liter, according to the equation:

$$Al_2(SO_4)_3.18H_2O + Na_2CO_3 + Pb(CH_3CO_2)_2.3H_2O = Al_2(SO_4)(CH_3CO_2)_2(OH)_2 + PbSO_4 + Na_2SO_4 + CO_2 + 21H_2O$$

(4) $Al_2(SO_4)(CH_3CO_2)(OH)_3$. 200g normal sulphate, 100.9g $NaHCO_3$, 61.1g 29 percent acetic acid per liter, according to the equation:

$$Al_2(SO_4)_3.18H_2O + 4NaHCO_3 + CH_3CO_2H = Al_2(SO_4)(CH_3CO_2)(OH)_3 + 2Na_2SO_4 + 4CO_2 + 19H_2O$$

(5) $Al_2(SO_4)(CH_3CO_2)(OH)_3$ as No. 4, but only 150g normal sulphate per liter.

TABLE B

Formula	Dissociation on heating			Dissociation on dilution	
	Start	At 100°	On cooling	Start	End
1. $Al_2(SO_4)(CH_3CO_2)_4$	89°	Jelly	Ppt. dissolves	—	—
2. $Al_2(SO_4)(CH_3CO_2)_3(OH)$	70°	Jelly	Ppt. almost dissolves	12 vols.	50 vols.
3. $Al_2(SO_4)(CH_3CO_2)_2(OH)_2$	52°	Jelly	Ppt. remains	4 vols.	24 vols.
4. $Al_2(SO_4)(CH_3CO_2)(OH)_3$	48°	Jelly	Ppt. remains	1 vol.	10 vols.
5. $Al_2(SO_4)(CH_3CO_2)(OH)_3$	40°	Jelly	Ppt. remains	$^3/_4$ vol.	7 vols.

Formula	Attraction of the fiber during mordanting and drying		
	Al_2O_3 presented to the fiber, grams	Al_2O_3 fixed by the fiber, grams	Percentage
1. $Al_2(SO_4)(CH_3CO_2)_4$	0.5750	0.5190	90.26
2. $Al_2(SO_4)(CH_3CO_2)_3(OH)$	0.5012	0.4957	98.90
3. $Al_2(SO_4)(CH_3CO_2)_2(OH)_2$	0.1851	0.1688	91.19
4. $Al_2(SO_4)(CH_3CO_2)(OH)_3$	0.1987	0.1914	96.33

From Table B it will be seen that with the sulpho-acetates of alumina any increase in basicity lowers the dissociation point both on heating and diluting with water. All these mordants yield nearly the whole of their alumina to the fiber during mordanting and drying, and act therefore much stronger than the sulphates.

"*Aluminum Acetates.*—The normal acetate was prepared by double decomposition of aluminum sulphate and lead acetate, and the basic acetates were made by adding sodium bicarbonate to solutions of the normal acetate. The following mordants, among others, were prepared:

(1) $Al_2(CH_3CO_2)_6$. 200g normal aluminum sulphate and 341.4g lead acetate per liter, according to the following equation:

$$Al_2(SO_4)_3.18H_2O + 3Pb(CH_3CO_2)_2.3H_2O = Al_2(CH_3CO_2)_6 + 3PbSO_4 + 27H_2O$$

(2) $Al_2(CH_3CO_2)_4(OH)_2$. 200g normal aluminum sulphate with 31.8g Na_2CO_3, and 227.6g lead acetate per liter, according to the following equation:

$$Al_2(SO_4)_3.18H_2O + Na_2CO_3 + H_2O + 2Pb(CH_3CO_2)_2.3H_2O = Al_2(CH_3CO_2)_4(OH)_2 + 2PbSO_4 + Na_2SO_4 + CO_2 + 24H_2O$$

(3) $Al_2(CH_3CO_2)_4(OH)_2$. 200g normal aluminum sulphate with 341.4g lead acetate per liter, and, after filtering, 50.5g $NaHCO_3$ added, according to the equation:

$$Al_2(CH_3CO_2)_6 + 2NaHCO_3 = Al_2(CH_3CO_2)_4(OH)_2 + 2CH_3CO_2Na + 2CO_2$$

(4) $Al_2(CH_3CO_2)_2(OH)_4$. 200g normal aluminum sulphate with 341.4g lead acetate, and 101g $NaHCO_3$ per liter, according to the following equation:

$$Al_2(CH_3CO_2)_6 + 4NaHCO_3 = Al_2(CH_3CO_2)_2(OH)_4 + 4CH_3CO_2Na + 4CO_2$$

TABLE C

Formula	Dissociation on heating			Dissociation on dilution	
	Start	At 100°	On cooling	Start	End
1. $Al_2(CH_3CO_2)_6$	—	—	—	—	—
2. $Al_2(CH_3CO_2)_4(OH)_2$	65.5°	Ppt. dense powdery	Ppt. remains	4 vols.	50 vols.
3. $Al_2(CH_3CO_2)_4(OH)_2$	74°	Ppt. dense powdery	Ppt. remains	—	—
4. $Al_2(CH_3CO_2)_2(OH)_4$	44°	Jelly	Ppt. remains	—	—

Formula	Attraction of the fiber during mordanting and drying		
	Al_2O_3 presented to the fiber, grams	Al_2O_3 fixed by fiber grams	Percentage
1. $Al_2(CH_3CO_2)_6$	0.2631	0.1349	51.27
2. $Al_2(CH_3CO_2)_4(OH)_2$	0.2213	0.2201	99.46

This series of experiments (Table C) shows also that increase in the basicity of aluminum acetate lowers the dissociation point on heating, but that by diluting with water they are not dissociated, not even when basic. Another series of experiments showed that the dissociation point of the basic acetate on heating was ever raised by dilution. The readier dissociation of No. 2 mordant is caused by the presence of Na_2SO_4. No. 4 mordant contains no Na_2SO_4. It is worthy of notice that the basic acetate deposits the whole of its alumina in the fiber, whereas the normal acetate gives up only half. Since the basic acetate experimented with contains sodium acetate, the authors purpose determining its influence in this respect.

"*Aluminum Sulphocyanates.*—These were prepared by double decomposition of barium sulphocyanate with normal aluminum sulphate, the basic ones being made by adding $NaHCO_3$ to the normal aluminum sulphocyanate. The following were prepared:

(1) $Al_2(SCN)_6$; (2) $Al_2(SCN)_4(SO_4)$; (3) $Al_2(SCN)_5(OH)$; (4) $Al_2(SCN)_4(OH)_2$; (5) $Al_2(SCN)_3(OH)_3$; (6) $Al_2(SCN)_2(OH)_4$

Contrary to statements which have been made that normal aluminum sulphocyanate solutions decompose when heated to 40°-50° C, it was found that they could be boiled even without decomposition, and only when evaporated over the naked fire to a syrupy consistency was there a slight separation of alumina. A solution of normal salt made from 200g aluminum sulphate per liter only yielded 33.37 percent of its alumina to the fiber by steeping and drying, much less, therefore, than in the case of all the mordants already tested in this respect with the exception of $Al_2(SO_4)_3$. With the exception of No. 3 mordant, which did not dissociate, all the basic sulphocyanates dissociate only on boiling, and increase of basicity simply renders the decomposition more complete. None are dissociated on diluting with water.

"*Aluminum Chlorides.*—Normal Al_2Cl_6 was prepared by dissolving aluminum hydrate in the calculated amount of HCl. Basic mordants were made by adding Na_2CO_3 to the normal solution. The following were prepared:

(1) Al_2Cl_6; (2) $Al_2Cl_5(OH)$; (3) $Al_2Cl_4(OH)_2$; (4) $Al_2Cl_3(OH)_3$; (5) $Al_2Cl_2(OH)_4$

None of these mordants dissociate either by heating or by diluting with water. The solubility of aluminum hydrate in Al_2Cl_6 was tested and the following results were obtained. To a solution of Al_2Cl_6 a quantity of aluminum hydrate was added sufficient to form the basic salt $Al_2Cl_4(OH)_2$. The alumina dissolved only on heating, and the solution remained clear on cooling. To this clear solution a further quantity of aluminum hydrate was added sufficient to form the compound $Al_2Cl_2(OH)_4$. It was, however, found that no more alumina could be made to dissolve, the precipitate even increasing, and on filtering it was found that the solution contained equal molecules of normal Al_2Cl_6 and of HCl. The nascent $Al_2Cl_2(OH)_4$ had apparently decomposed according to the following formula:

$$7Al_2Cl_2(OH)_4 + 2H_2O = 5Al_2(OH)_6 + 2Al_2Cl_6 + 2HCl$$

In the same way it was found that, on adding aluminum hydrate to $Al_2(SO_4)_3$ solution sufficient to produce the basic compound $Al_4(SO_4)_3(OH)_6$, no alumina at all dissolved, the filtrate only containing $Al_2(SO_4)_3$. Here, too, we must suppose that the nascent basic compound decomposes as follows:

$$Al_4(SO_4)_3(OH)_6 = Al_2(OH)_6 + Al_2(SO_4)_3$$

Because of the excellent results in the steam alizarine reds yielded by the following mordant its dissociation qualities and behavior to the cotton fiber were ascertained. The mordant is an aluminum-chloride-acetate, $Al_2Cl_2(CH_3CO_2)_4$ prepared according to the following equation:

$$Al_2(SO_4)_3.18H_2O + 2Pb(CH_3CO_2)_2.3H_2O + BaCl_2 + 2H_2O = \\ Al_2Cl_2(CH_3CO_2)_4 + BaSO_4 + 2PbSO_4 + 26H_2O$$

200g normal aluminum sulphate, 227.6g lead acetate, and 73.3g barium chloride were dissolved in one liter of water. This mordant dissociated neither on heating nor on diluting with water, and yields to the cotton fiber the remarkably low amount of 3.26 percent alumina.

"*Aluminum Nitrates.*—The normal salt was prepared in solution by double decomposition of normal aluminum sulphate with lead nitrate. Basic mordants were prepared by addition of $NaHCO_3$ to the normal mordant. The following mordants were prepared:

(1) $Al_2(NO_3)_6$; (2) $Al_2(NO_3)_5(OH)$; (3) $Al_2(NO_3)_4(OH)_2$; (4) $Al_2(NO_3)_3(OH)_3$; (5) $Al_2(NO_3)_2(OH)_4$

All the solutions corresponded to 200g normal sulphate per liter water. None of these mordants dissociated either on heating or diluting with water.

"*Aluminum Phosphate in Solution.*—It was ascertained, contrary to the statements appearing in textbooks, that sodium phosphate, Na_2HPO_4, produces no permanent precipitate in presence of an excess of $Al_2(SO_4)_3$. It was further proved by experiment that two molecules of $Al_2(SO_4)_3$ are the smallest quantity which is capable of retaining one molecule of $Al_2(PO_4)_2$ in solution."

The first point to be considered in regard to this paper is whether these basic salts represent anything more than the ratio of added sodium salt to the aluminum salt in solution. Liechti and Suida evidently believe that they are dealing with dissolved basic salts which are definite compounds. Though they do not so state it, their course of reasoning evidently is that alumina is insoluble in water, that alumina did not precipitate, and that, therefore, a soluble basic salt must have been formed. The flaw in the reasoning is the assumption that the alumina must precipitate because it is insoluble. It may stay in apparent solution as colloidal alumina. It is, therefore, very much of a question what one has in the case of a solution of any aluminum salt. In Thorpe's Dictionary of Applied Chemistry,[1] I find the statement that "the triacetate or normal [aluminum] acetate $Al_2(CH_3CO_2)_6$ is not known. A solution corresponding to this compound, but which appears to be a mixture of the diacetate and acetic acid, is the only acetate of commercial importance. It is known as 'red liquor' or 'mordant rouge,' and is largely used in dyeing and calico printing, especially for the production of red colors, madders and pinks (whence its name of red liquor); for the production of dense lakes, and for waterproofing woolen fabrics."

No one would guess the non-existence of the normal acetate from anything in Liechti and Suida's paper, and yet

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[1] "Dictionary of Applied Chemistry," 2nd Ed., 1, 14 (1912).

Crum[1] was familiar with the fact. "On the question, as to which of the soluble acetates of alumina can be considered as a definite compound, it has already been stated of the teracetate, that when evaporated rapidly enough, and at a heat just low enough to prevent the formation of the insoluble salt, it leaves a product whose composition is nearly that of a binacetate. It may be added that the solution of teracetate gives off acetic acid as freely in the cold, as if a third part of its acid were free. On making an experiment with two solutions of acetate of lead—one of which was decomposed by sulphuric acid and the other (which was three times as strong) by tersulphate of alumina—it was found that the aluminous solution gave a smell of acetic acid considerably stronger than that in which the acid was known to be free. It may be doubted, then, whether there exists a combination of acetic acid with alumina corresponding to the tersulphate of alumina. The solution of binacetate has no smell of acetic acid at ordinary temperatures."

Crum considers that the diacetate, $Al(CH_3CO_2)_2OH$ or $Al_2(CH_3CO_2)_4(OH)_2$, is a definite compound, and this view has been held by all other writers since his time. It is an open question whether this is correct or not because there is said to be a soluble and an insoluble form of the so-called diacetate. This in itself sounds like a case of colloidal suspension and of coagulation. However this may be, Crum's work on colloidal alumina[2] shows that one cannot draw any conclusion as to the existence of definite compounds from the fact that no visible precipitation occurs.

"By the continued action of heat on a weak solution of binacetate of alumina, a permanent separation of the constituents of the salt takes place, although no acid escapes, and no alumina is precipitated. The properties of the alumina are at the same time materially changed. A solution of binacetate of alumina, diluted so as to contain not more than

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[1] Jour. Chem. Soc., 6, 224 (1854).

[2] Crum: Ibid., 225 (1854).

1 part of alumina in 200 of water, was placed in a close vessel which was immersed to the neck in boiling water, and kept in that state day and night for ten days. It had then nearly lost the astringent taste of alum, and acquired the taste of acetic acid. Being afterwards boiled in an open capsule acetic acid was freely given off, and when the boiling had continued about five hours (the loss of water being continually restored), the liquid was found to have retained not more than $^1/_{11}$ of its original quantity of acetic acid, or about 1 equiv. to $5^1/_2$ of alumina.

"The solution of hydrate of alumina thus obtained has nearly the same transparency as before the loss of its acid, and is slightly oily. It is nearly tasteless. By longer boiling it may be deprived of considerably more of its acid, but there is a danger of coagulation. A solution containing $^1/_4$ percent of alumina is converted into a solid transparent jelly, when mixed with half its bulk of water acidulated with $^1/_{2500}$ of sulphuric acid. The jelly has, therefore, only $^1/_{600}$ of its weight of alumina, and $^1/_{7500}$ of sulphuric acid. By pressure in a bag the liquid part of this jelly was readily separated, and the solid was reduced to $^1/_{60}$ or $^1/_{70}$ of its original volume. Pure water did not dissolve this residue, neither did an excess of sulphuric acid, even at a boiling heat. On examination it was found that the solid portion had imbibed almost the whole of the sulphuric acid. It existed there in the proportion of about 1 equiv. of acid to 15 of alumina.

"The coagulating power of the various agents may be ascertained with tolerable accuracy by employing an aluminous solution so dilute as to contain not more than 1 part of alumina in 800 of water, and shaking it in a phial with about half its volume of a coagulating solution. In this manner it was found that 1 atom of citric acid (tribasic) coagulates as powerfully as 3 atoms of sulphuric acid, and tartaric acid (bibasic) as much as 2. Two atoms of oxalic acid are required to produce the same effect as 1 of sulphuric acid. Of muriatic and nitric acids, not less than 300 equiv. must be employed to produce an effect equal to that of 1 equiv. of sulphuric acid

—the volume of the acid being always half that of the aluminous solution. No acid has the power of redissolving the coagulum.[1]

"The alkalies have a strong coagulating power. About 2 equivs. of potash produce an effect equal to 1 of sulphuric acid, and the same is the case with soda, ammonia, and lime. The coagulation takes place before the acetic acid which remains in the aluminous solution is fully saturated; for when the alkali, in a very dilute state, is added with caution, the coagulum which it produces has still an acid reaction. This coagulum, like that from sulphuric acid, is insoluble in any acid, whether cold or hot, as well as in pure water. It dissolves, however, in a boiling solution of potash or soda, and when the alkaline solution is afterwards saturated by an acid, the ordinary terhydrate of alumina is thrown down. Large quantities, however, of the acetic salts (already formed) may be added before they coagulate the aluminous solution.[2] When the solid part of the coagulum produced by a strong solution of acetate of soda was afterwards freed from that salt by pressure, it redissolved in pure water, and the solution was again coagulated by a fresh addition of the salt. An experiment with acetate of lime gave the same result. The nitrates and chlorides coagulate also with great difficulty.

"Solutions of sulphate of soda, magnesia, and lime coagulate as readily as a liquid containing the same quantity of sulphuric acid in the free state. On examining one of these mixtures, the sulphuric acid was found in the solid part of the coagulum as before, and the alkali in the fluid part, united with the acetic acid which had remained in the aluminous solution after boiling. The digested solution of alumina,

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[1] Since these experiments were concluded, it has been found that by employing a wider and shallower porcelain vessel, it is possible to boil off, in an hour and a half, a much larger proportion of acetic acid than that which is mentioned in the text as being done in five hours; and to obtain a product equally fluid.

[2] Hence, in preparing the binacetate of alumina, which is to be used in obtaining the bihydrate, it is better to employ an excess of acetate of baryta, than to leave in the solution the slightest trace of sulphuric acid.

which has not been deprived of its acetic acid by boiling, requires about twice as much sulphuric acid to coagulate it as does the boiled solution, and thirty or forty times as much alkali. The coagulation is complete before the acetic acid is entirely saturated. One of the most characteristic properties of the digested and altered acetate of alumina is its loss of the power of acting as a mordant. The ordinary acetate, as is well known, forms a yellow opaque precipitate with decoction of quercitron. That which has been thoroughly digested is merely coagulated by the decoction—the color of which is but little altered, and the coagulum is translucent. The same effect is produced with decoctions of logwood, brazilwood, etc....

"It has been already mentioned that when the precipitated [insoluble] binacetate is kept for an hour or two in 200 parts of boiling water, it is changed into the soluble binacetate. The substance so produced may be converted, like the original solution, into the peculiar bihydrate. Thirty to thirty-six hours' digestion is sufficient to complete the change, for after that time the solution has no longer any taste of alum, and the power of coagulating with acids does not increase. A portion of it was boiled in an open vessel eleven hours, being retained at the strength of $^1/_2$ percent of alumina by successive additions of water. The solutions remained quite clear, and became very slightly oily. It then contained only about 1 equiv. of acetic acid to 19 of alumina. This preparation may be considered as free from all other foreign matter, with the exception of a trace of iron, which still adheres to it. As compared with the solution prepared at once from the soluble binacetate, smaller quantities of the reagents are sufficient to coagulate it, and the coagulum produced has not more than half the density. 0.03g of sulphuric acid, or 0.06g of sulphate of soda is sufficient to coagulate 1.5g of alumina in 600g water, being in the proportion of about 1 equiv. of sulphuric acid to 35 of alumina. An equal quantity of the solution was completely coagulated by 0.034g of potash and by 0.020g of ammonia. In both of these experiments the acetic acid was not fully saturated. The alkalies then are equivalent in coagulating power to sulphuric acid when a very small quantity only of acetic acid is present in the solution. . . .

"It is well known that when teracetate of alumina is boiled along with sulphate of potash, a gelatinous precipitate is formed, which redissolves when the solution becomes cold. M. Koechlin-Schouch found it to be a subsulphate of alumina. When alum, dissolved in six times its weight of water, was treated with 3 equiv. of acetate of lead—enough to decompose its tersulphate of alumina, but not the sulphate of potash—a large proportion (74 percent) of the sulphate of potash was found to be carried down by the sulphate of lead formed in the process. To a solution so prepared, the loss was restored by an addition of sulphate of potash, and a mixture formed of

KO_2SO_3 together with $Al_2O_3.3\ddot{A}$.

This solution, diluted so as to contain about 0.3 percent of alumina (from 5 oz. of alum per gallon), was exposed to heat. At about 90° Fahr., the gelatinous precipitate began to form; and after two hours' boiling, when scarcely a trace of alumina remained in solution, it was thrown upon a filter of calico, which was kept hot within a steam-pan until the filtrate passed through. The collected precipitate was pressed between numerous folds of bleached calico, and brought up gradually to the state of a stiff clay occupying no more than $^1/_{10}$ of the volume of the original solution. It was then divided into portions which could conveniently be shaken and thoroughly mixed in bottles with quantities of water equal in all to the original solution. The mixture was filtered as before and pressed between folds of calico; and another repetition having been made of the same process, the precipitate was deprived of every admixture of soluble matter.

"A portion being dissolved in nitric acid and filtered, gave an abundant precipitate with nitrate of baryta. Exposed to a white heat, and the residue pulverized and boiled in water, the filtered liquor gave no longer a precipitate with nitrate of baryta, and no indication, or a very doubtful one, of alkali to litmus paper; proving that the sulphuric acid indicated by the first test had been combined, not with potash, but with alumina. Mixed with sulphuric acid, the substance gave no smell of acetic acid, and when burned with oxide of copper it yielded no more carbonic acid than could readily be accounted for by the few fibers of cotton-wool that were to be distinguished in the liquid. The substance dried into a hard, whitish, semi-transparent matter, easily pulverized."

An analysis of this product gave results agreeing very well with the formula $Al_4O_5SO_4.10H_2O$ and Crum assumes that he actually has this basic salt. While this is possible, it is not proved, and one is rather sceptical about it in view of the fact that three slightly differing methods of preparation gave varying percentages of alumina, 43.51, 44.16, and 50.71. Crum[1] also found that a solution of so-called aluminum acetate is precipitated by sodium chloride.

"A solution of teracetate of alumina was produced from 1 pound of acetate of lead in 10 pounds of water, decomposed by tersulphate of alumina. After purification, common salt was added to it in the proportion of 1 equiv. to 1 of tersulphate of alumina. The solution, when heated in the water bath, became of an opaque white from the deposition of a powder so very fine that the mixture passed through the filter almost without change. Neither heat nor any other application could alter this character. It was left at rest, and after some weeks, the liquid, having become nearly clear, was poured off, and the precipitate, which had contracted into $^1/_{64}$ of the bulk of the liquid was mixed again with fresh water 11 times its volume. After several weeks more the precipitate fell again to the bottom of the vessel, when it was mixed with a third portion of the fresh water, which again, after four weeks, was decanted, and the precipitate dried in a capsule at 100° Fahr."

On analysis the product was found to contain acetate,

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[1] Crum: Jour. Chem. Soc., 6, 231 (1854).

chloride and sodium even after all this washing. Crum states very frankly that he could not make a formula which could be stated in atomic proportions. It is quite clear that the precipitate was alumina which had adsorbed some acetic acid, some hydrochloric acid, and some sodium chloride.

Graham[1] has confirmed these results of Crum. "We are indebted to Mr. Walter Crum for the interesting discovery that alumina may be held in solution by water alone in the absence of any acid. But two soluble modifications of alumina appear to exist, alumina and metalumina. The latter is Mr. Crum's substance. A solution of the neutral chloride of aluminum (Al_2Cl_3) placed on the dialyser, appears to diffuse away without decomposition. But when an excess of hydrated alumina is previously dissolved in the chloride, the latter salt and free hydrochloric acid are found to escape by diffusion in a gradual manner, and the hydrated alumina, retaining little or no acid, to remain behind in a soluble state. A solution of alumina in chloride of aluminum, consisting at first of 52 parts of alumina to 48 of hydrochloric acid, after a dialysis of six days, contained 66.5 percent of alumina; after eleven days 76.5 percent; after seventeen days 92.4 percent, and after twenty-five days the alumina appeared to be as nearly as possible free from acid, as traces only of hydrochloric acid were indicated by an acid solution of nitrate of silver. But in such experiments the alumina often pectizes in the dialyser before the hydrochloric acid has entirely escaped. Acetate of alumina with an excess of alumina gave similar results. The alumina remained fluid in the dialyser for twenty-one days, and when it was pectized was found to retain 3.4 percent of acetic acid, which is in the proportion of 1 equivalent of acid to 28.2 equivalents of alumina.

"Soluble alumina is one of the most unstable of substances,[2] a circumstance which fully accounts for the difficulty of pre-

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[1] Phil. Trans., 151, 207 (1861); Jour. Chem. Soc., 15, 247 (1862).

[2] [This refers to the highly purified substance. It is possible that Liechti and Suida considered that the statement applied to all solutions containing an excess of base.]

paring it in a state of purity. It is coagulated or pectized by portions, so minute as to be scarcely appreciable, of sulphate of potash and, I believe, by all other salts; and also by ammonia. A solution containing 2 or 3 percent of alumina was coagulated by a few drops of well-water, and could not be transferred from one glass to another without gelatinizing; unless the glass was repeatedly washed out by distilled water. Acids in small quantity also cause coagulation; but the precipitated alumina readily dissolves in an excess of the acid. The colloids gum and caramel also act as precipitants.

"This alumina is a mordant, and possesses indeed all the properties of the base of alum and the ordinary aluminous salts. A solution containing 0.5 percent of alumina may be boiled without gelatinizing, but when concentrated to half its bulk, it suddenly coagulated. Soluble alumina gelatinizes when placed upon red litmus paper, and forms a faint blue ring about the drop, showing a feeble alkaline reaction. Soluble alumina is not precipitated by alcohol or by sugar. No pure solution of alumina, although dilute, remained fluid for more than a few days. Like hydrated silicic acid, then, the colloid alumina may exist either fluid or pectous, or it has a soluble and insoluble form, the latter being the gelatinous alumina as precipitated by bases. It is evident that the extraordinary coagulating action of salts upon hydrated alumina must prevent the latter substance from ever appearing in a soluble state when liberated from combination by means of a base.

"Colloidal alumina possesses also, I believe, a high atomic weight, like cosilicic acid. The chloride of aluminum with excess of alumina referred to above appears to be, either in whole or in part, a colloidal hydrochloride of alumina, containing the latter substance with its large colloidal equivalent, and may be really neutral in composition. The soluble persalts of iron, tin, etc., are likewise all colloidal, and have no doubt a similar constitution. Such colloidal salts are themselves slowly decomposed on the dialyser, being resolved into the crystalloidal acid which escapes and the colloidal oxide which remains behind.

"*Soluble Metalumina.*—Mr. Crum first pointed out a singular relation of acetic acid to alumina, which has never been explained. Sulphate of alumina, when precipitated by acetate of lead or baryta, gives a binacetate of alumina, with one equivalent of free acetic acid, the neutral teracetate of alumina not appearing to exist. It was further observed that, by keeping a solution of this binacetate in a closed vessel at the boiling point of water for several days, nearly the whole acetic acid came to be liberated, without any precipitation of alumina occurring at the same time. Mr. Crum boiled off this free acetic acid, or the greater part of it, and thus obtained his soluble alumina. The same result may be obtained by dialysing a solution of acetate of alumina that has been altered by heat. In three days the acetic acid was reduced on the dialyser to 11 percent, giving 1 equiv. acetic acid to 8 equiv. alumina; in six days to 7.17 percent acid; in thirteen days to 2.8 percent acid, or 1 equiv. acid to 33 equivs. alumina. The alumina exists in an allotropic condition, being no longer a mordant; and forming, when precipitated, a jelly that is not dissolved by an excess of acid. Metalumina resembles alumina in being coagulated by minute proportions of acids, bases, and of most salts. Mr. Crum found the solution of metalumina to require larger quantities of acetates, nitrates, and chlorides to produce coagulation than of sulphates. The solution of metalumina is tasteless, and entirely neutral to test paper, according to my own observation. Like alumina, the present colloid has therefore a fluid and a pectous form, the liquid soluble metalumina, and the gelatinous insoluble metalumina."

Liechti and Suida[1] commented on the fact "that the basic acetate precipitated the whole of its alumina in the fiber whereas the normal acetate gives up only half." This is not due to any property belonging exclusively to the fiber.

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[1] Jour. Soc. Chem. Ind., 2, 539 (1883).

Graham[1] notes that "to facilitate the separation of hydrochloric acid from the perchloride of iron, for instance, that salt is first rendered basic by the addition of peroxide of iron. The comparatively stable perchloride of iron is transformed by such treatment, into a feebly constituted colloidal hydrochloride. The latter compound breaks up under the purely physical agency of diffusion, and divides on the dialyser into colloidal peroxide of iron and free hydrochloric acid."

The same thing apparently takes place with chromic chloride though it is not stated so definitely.[2] "The definite terchloride of chromium, being a crystalloid, diffuses away entirely when placed in solution upon the dialyser. This salt dissolves, with time, a certain portion of freshly precipitated hydrated chromic oxide, and becomes of a deeper green color. Such a solution, after dialysis for twenty-two days, contained 8 hydrochloric acid to 92 chromic oxide; and after thirty days, 4.3 acid to 95.7 oxide, or 1 equiv. acid to 10.6 equivs. oxide. After thirty-eight days, the solution gelatinized in part upon the dialyser and then contained 1.5 acid to 98.5 oxide, or 1 equiv. acid to 31.2 equivs. chromic oxide. This last solution, which may be taken to represent soluble chromic oxide, is of a dark green color, and admits of being heated, and also of being diluted with pure water without change. It was gelatinized with the usual facility by traces of salts and other reagents which affect colloid solutions, and was then no longer soluble in water, even with the assistance of heat. It appeared to be the green hydrated oxide of chromium, as that substance is usually known. A metachromic oxide may possibly be obtained by heating and dialysing the acetate, but I have not attempted to form it."

Tommasi[3] has studied the action of aluminum on cupric chloride. "Aluminum acts rapidly, even at ordinary temperatures, on a solution of cupric chloride, with liberation

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[1] Jour. Chem. Soc., 15, 265 (1862).

[2] Graham: Ibid., 15, 254 (1862).

[3] Bull. Soc. chim. Paris, [2] 37, 443 (1882); Jour. Chem. Soc., 44, 19 (1883).

of hydrogen and copper, and formation of an aluminum oxychloride, the composition of which depends on the concentration of the copper solution. With a 31.25 percent solution of cupric chloride, the aluminum oxychloride had the composition $2Al_2O_6H_6.3Al_2Cl_6$, and with a 7.81 percent solution, the composition $Al_2O_6H_6.4Al_2Cl_6$. These oxychlorides are easily decomposed and will not crystallize. They are not true compounds, but variable mixtures of aluminum chloride and oxychloride. The action of metallic aluminum on these oxychlorides yields as a final product the compound $Al_2Cl_6.6Al_2O_6H_6.12H_2O$. To obtain this compound, a 31.25 percent solution of cupric chloride is treated with aluminum until all the copper is precipitated; the liquid is filtered, the filtrate heated, and aluminum added in successive small quantities until it ceases to dissolve, water being added from time to time to make up for evaporation. The clear liquid is then evaporated to a syrup, and finally dried at 40°-50°. In this way the oxychloride is obtained in white flakes resembling those of potassium boro-tartrate. A solution of this oxychloride, like that of ferric oxychloride, is precipitated by sulphuric acid and by certain salts, such as the sulphates of sodium, ammonium, potassium, magnesium, zinc, copper, and iron; but it is not precipitated, even on boiling, by the chlorides of potassium, ammonium, sodium, copper, or barium, by potassium iodide, potassium bromide, ammonium nitrate, or potassium bromide. The aluminum hydroxide thrown down is but slightly soluble in sulphuric acid, and appears to be an isomeric modification, probably the modification δ, described[1] by the author."

There is no proof for the statement that the oxychlorides of varying composition are mixtures of aluminum chloride and of a definite oxychloride; and there is no proof that there is any definite oxychloride. The fact that the so-called oxychloride is precipitated by sulphate is what one would expect of a colloidal suspension and is not characteristic of a true

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[1] Tommasi: Comptes rendus, 91, 231 (1880).

solution. It is probable, therefore, that we are dealing entirely with adsorption phenomena. Schneider[1] also gives experiments which show that a solution of aluminum chloride really contains some or all of the alumina in colloidal suspension. "It is a familiar fact[2] that traces of sulphuric acid precipitate alumina from solutions of basic aluminum chloride. I think that it is new that acid aluminum chloride solutions are coagulated by sulphuric acid. Addition of a trace of sulphuric acid to an acid aluminum chloride solution containing 0.1894g alumina in 400 cc (1 mol Al_2O_3, to 7.2 mol HCl) caused the precipitation of 0.0486g alumina, or 25.6 percent of the total alumina.

"I have also found it stated in the textbooks that the solubility of alumina in acids decreases if the alumina is allowed to stand a long time under a solution of ammonia. I have not found any reference to the fact that when an aluminum chloride solution is formed by dissolving in hydrochloric acid an alumina which had stood for a long time under aqueous ammonia, the addition of sulphuric acid causes a greater precipitation than when the solution is prepared from alumina which has been freshly precipitated with ammonia."

This last statement would be quite impossible if we were dealing with a true solution. It is quite natural if we consider that Schneider was really peptonizing alumina with hydrochloric acid and that he was peptonizing a more hydrous, or less dense, alumina in one case than in the other. It is the same difference that we have on precipitation, Graham's method giving so-called alumina while Crum's method gives so-called metalumina. I shall come back to this again when I come to the question of burned mordants.

Müller[3] has shown definitely that an alumina hydrosol is obtained by peptonizing freshly precipitated alumina with

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[1] Ber. chem. Ges, Berlin, 23, 1353; Liebig's Ann., 257, 368 (1890).

[2] Ordway mentions that basic aluminum chloride solution precipitates alumina on addition of small amounts of sulphuric acid (Am. Jour. Sci., [2] 26, 203 (1858)).

[3] Zeit. anorg. Chem., 57, 311 (1908).

$N/20$ hydrochloric acid. "That we are dealing with colloidal hydrosols is proved by the behavior of these solutions. They are microscopically homogeneous and resemble other colloidal sols by passing readily through filter paper. The effect of electrolytes is typical. Dilute solutions of univalent acids or of salts with univalent cations may be added without producing important changes. Acids with multivalent anions and salts of these acids (sulphuric acid and sulphates, for instance) cause the coagulation of a gelatinous hydrogel even when added in very small amounts." Müller[1] also points out that the "basic aluminum salts" obtained by Ordway[2] and others are mythical.

From all this evidence we are justified in concluding that aluminum salts hydrolyze more or less completely when dissolved in water. This change takes place slowly at low temperatures and more rapidly when the solutions are heated. The reaction products are colloidal alumina and free acid; there is no satisfactory evidence of the formation of any basic salts in solution though the absolute non-existence has also not been proved. With aluminum acetate the hydrolysis takes place so rapidly that it seems certain that no appreciable amount of the normal acetate is formed when equivalent solutions of aluminum sulphate and lead acetates are mixed. Liechti and Suida were certainly not working with the basic salts which they thought they were studying. Since they made up their solutions synthetically and did not analyze after filtering, it seems possible that none of the solutions had the composition that Liechti and Suida have given. Since lead sulphate may carry down as much as 74 percent of the potassium sulphate from a potash alum solution,[3] it is unsafe to assume that nothing is carried down from an aluminum sulphate solution.

Liechti and Suida's experiments on the dissociation of aluminum sulphate solutions are just what one would ex-

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[1] Zeit. anorg. Chem., 57, 320 (1908).

[2] Am. Jour. Sci., [2] 26, 203 (1858).

[3] Crum: Jour. Chem. Soc., 6, 229 (1854).

pect (Table A). With increasing addition of sodium carbonate, a precipitate is formed more readily both on heating and on dilution. The more dilute solution, No. 3, coagulates more readily than the more concentrated one, No. 2. The sulpho-acetates, Table B, also behave as they should. The hydrolysis proceeds farther with a weaker acid, acetic acid, than with sulphuric acid and there is enough sulphate present to act as a coagulating agent. The sulpho-acetates are more readily decomposed both on heating and on dilution than the corresponding sulphate solutions. The acetates, Table C, do not coagulate on dilution, presumably owing to the absence of a precipitating agent. No. 2 solution seems an exception but the reason for this was pointed out by Liechti and Suida though they did not understand it. This solution contained sodium sulphate. I have not been able to find any special experiments on the effect of sulphocyanates on colloidal alumina. To account for the fact as noted by Liechti and Suida, one must assume that sulphocyanates have a lesser precipitating power or a greater peptonizing power than acetates. This assumption is a plausible one because we find that acetates come between sulphates and sulphocyanates in their action on gelatine and on albumin.[1] The chlorides, chloride-acetates, and nitrates of aluminum all behave as they should in view of what was shown by Crum in regard to the coagulating action of the various acid radicals. If we wanted any further proof that we are not dealing with definite basic salts, we could find it in the fact that Liechti and Suida were able to prepare what they called $Al_2Cl_2(OH)_4$ by adding sodium carbonate to an aluminum chloride solution but were not able to go beyond what they called $Al_2Cl_4(OH)_2$ by dissolving alumina in aluminum chloride. Of course this is not absolutely conclusive because Liechti and Suida did not add sodium chloride to the second solution and consequently the solutions were not strictly comparable; but this difference is probably not of much importance.

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[1] Freundlich: Kapillarchemie, 418, 425 (1909).

Liechti and Suida's experiments on the behavior of solutions of aluminum salts in presence of cotton are very disappointing. They had the right idea in making up most of the solutions to contain the same amount of alumina per liter; but, after that, they seem to have gone all to pieces and to have tried to make their experiments as little comparable as possible. Instead of leaving the cotton in the solution until equilibrium was reached, they impregnated the cotton with an alum mordant until its weight was exactly doubled. Heermann[1] showed that with silk "the maximum increase in weight (fiber and mordant) is reached after periods of mordanting ranging from six hours to two days," the salts used being those of tin, iron, chromium, and aluminum. While it is not legitimate to assume that cotton would behave exactly like silk, the very fact that Liechti and Suida took pains to stop the treatment when the weight was exactly doubled, shows that they did not await equilibrium. The experiments in any single series are therefore not comparable and the different series are not comparable because Liechti and Suida determined the amount of alumina fixed on the fiber after drying in a constant air current for six hours at 40°. This may of course give results with a volatile acid like acetic acid which dffer from those obtained with sulphuric acid. As might be expected, one can draw any conclusions one likes from the experiments. In Table A the percentage alumina fixed on the fiber increases from 12.9 with aluminum sulphate to 51.0 with so-called $Al_2(SO_4)_2(OH)_2$, and to 58.7 with so-called $Al_4(SO_4)_3(OH)_6$. From this Liechti and Suida draw the conclusion that the more basic the mordant, the greater is the proportion of alumina fixed on the fiber by steeping, hanging, and drying. The absolute amounts of alumina fixed on the fiber are shown by Table A to be 0.0901g, 0.2283g, and 0.0897g from which we could draw the conclusion that more alumina is fixed from a moderately basic mordant than from one that is either more or less basic. When we look up in

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[1] Jour. Soc. Chem. Ind., 22, 361 (1903).

Table A the total amount of alumina taken up by the fiber while the cotton is doubling in weight, we find that the figures are 0.6971g, 0.04473g and 0.1527g from which we could conclude that alumina is taken up (not fixed) more rapidly the less basic the mordant. These three sets of conclusions show how futile the experiments of Liechti and Suida are so far as giving us any real information. The matter is almost equally bad with the sulpho-acetates, Table B. With the most basic mordant the percentage of alumina fixed is 96.3 as against 90.3 with the least basic but the absolute amount fixed is 0.1914g with the most basic mordant and 0.5180g with the least basic. In all the cases where acetate and sulphate are both present in the solution, Tables B and C, the percentage alumina fixed by the fiber varies between 90 and 99. In the only case in which a straight acetate mordant was used the percentage alumina fixed was only 51. No experiments are therefore available on a basic acetate mordant containing no sulphate. It is difficult to see of just what use Liechti and Suida's experiments with cotton are.

The question as to the form in which mordants are taken up has been answered by Heermann[1] for the case of silk. "Raw and boiled-off silks which had been mordanted at 30° with stannic chloride, basic ferric sulphate, chromic chloride, and aluminum acetate were examined with a view to ascertaining in what form the mordant was present in the fiber. The silk was mordanted, washed thoroughly with water, and titrated directly with standardized sodium hydroxide solution; this method gives a direct determination of the amount of acid radical present in the mordanted fiber in the form of basic salt; its accuracy was checked by fusing the fiber with alkali hydroxide, and determining the amount of acid radical in the usual manner. A deduction was necessary from these results since traces remain adhering mechanically to the fiber, even after most careful washing, and this was ascertained by substituting for the mordanting a treatment with a solution

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[1] Jour. Soc. Chem. Ind., 23, 1143 (1904).

of the acid of which the radical was present in the mordant, the other conditions of the process, and the analytical method being the same as above. It was found that considerable range in the concentration of the acid solution used has no effect on the amount of acid adhering to the fiber; *e. g.*, treatment with 1, 5 and 10 percent solution of hydrochloric acid resulted in the same percentage of acid being retained in each case. The analytical data were completed by a determination of the amounts of metallic oxide present in the fiber. The results were as follows: in the case of the tin mordant, the raw silk was found to contain 155 mols of stannic oxide to each atom of chlorine, corresponding to a formula of $SnCl_4.619Sn(OH)_4$, and a basicity number of 0.0019; boiled-off silk contained 143 mols of stannic oxide to each atom of chlorine, corresponding to $SnCl_4.571Sn(OH)_4$ and a basicity number 0.0021. With the iron mordant on raw silk, 111 mols of ferric oxide were present to each mol of SO_3, *i. e.*, $Fe_{222}SO_3OH_{664}$, basicity number 0.008; on boiled-off silk, 91 mols Fe_2O_3 to 1 mol of SO_3, or $Fe_{182}SO_3(OH)_{544}$, basicity number 0.0096. Chromium mordant on raw silk, 40 mols of chromic oxide to 1 atom of chlorine, or $Cr_{80}Cl(OH)_{239}$, basicity number 0.009; on boiled-off silk, 44 mols of Cr_2O_3 to each atom of chlorine, or $Cr_{88}Cl(OH)_{203}$, basicity number 0.008. Aluminum mordant; in neither raw nor boiled-off silk could any acid radical be detected, showing that the aluminum was present as hydroxide. It would thus appear that for all practical purposes, the mordant is not present in the fiber in the state of a basic salt, but in the form of the hydroxide."

We do not seem to have corresponding data for cotton; but there seems to be good reason for assuming that the basic mordants really are the hydrous oxides[1] proper and are not, in general, basic salts.

Heermann[2] has also studied the effect of temperature on the amounts of various mordants taken up by silk. "Silk

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[1] Cf. Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 2nd Ed., 234 (1910).

[2] Jour. Soc. Chem. Ind., **22**, 623 (1903); **23**, 57 (1904).

was mordanted for six hours at temperatures ranging from 0° to 30° C, at intervals of 5° with tin, iron, chromium, and aluminum mordants. At temperatures between 0° and 5°, iron and chromium mordants were adsorbed with great difficulty; tin mordants slightly more easily. With iron and tin mordants, the temperature has practically no effect on the amount adsorbed by boiled-off silk, but the amount adsorbed by raw silk increases considerably with the temperature, reaching a maximum at 30°. Chromium mordants act in just the reverse manner, *viz.*, the temperature has no effect on mordanting raw silk; but boiled-off silk adsorbs more of the mordant as the temperature rises; with aluminum mordants, raw and boiled-off silks adsorb increasing quantities up to 20°, when a maximum is reached." "It is found that at low temperatures, 0°-5°, the penetration of the fiber (previously moistened with water) by the mordanting salts and the adsorption by it of metallic oxides take place slowly and with difficulty, owing to the reduction in the power of diffusion of the salts in solution at such temperatures. Hence the silk tends to become unevenly mordanted. At 15°-20° the fiber is penetrated with ease by the salts, and mordanting takes place more regularly."

We can now consider some of the problems that come up in the actual mordanting of wool.[1] "Wool differs essentially from cotton in its behavior toward the aluminum salts and is mordanted in a totally different way. The investigations of Liechti and Schwitzer[2] have thrown much valuable light on the reactions which take place in mordanting wool. Experiments have shown that wool takes up sulphuric and hydrochloric acids in the free state, retaining them with such force that they are only imperfectly removed by repeated boiling out with water. In a similar manner salts are taken up. The wool fiber possesses both basic and acid character, and seems to dissociate the salt by combining both with

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[1] Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 2nd Ed., 236 (1910).

[2] Jour. Soc. Chem. Ind., 5, 526 (1886).

the acid and with the base, the base being taken up either in the free state or in the form of a basic salt. This reaction takes place most completely at the boiling point. Aluminum sulphate, for instance, is most readily decomposed by the wool fiber into basic sulphates and free acid, especially at or near the boiling temperature. The alumina which is thus taken up is retained in an insoluble form with considerable force by the fiber; no fixing agents are required as in the case with cotton; the fixation takes place simultaneously with the impregnation in the mordanting bath under the influence of the elevated temperature. The basic salts, which are fixed on the fiber, undergo a further decomposition by washing with water; they lose acid, and become more basic, while the acid is removed by the wash water.

"The wool fiber attracts, also, finely-divided precipitates from liquids, and retains them with great energy. This power of attraction is comparatively weak in cold liquids, but it increases with the temperature, so that considerable amounts of such precipitates can be attached to the wool by prolonged boiling, although not fast enough to resist washing and rubbing. By the action of the wool fiber on aluminum sulphate a precipitate of basic aluminum sulphate may be produced and boiled on to the wool fast enough to resist washing with water, although it is only mechanically fixed on the surface of the fiber. These superficially fixed mordants produce, in dyeing, color lakes, which adhere still more loosely to the surface of the fiber, and possess in a high degree the defect of rubbing.

"On the contrary, mordants which have entered into an intimate combination with the substance of the fiber are less liable to produce color lakes which rub off. To attain this end the mordanting salt must possess a certain resistance to the dissociating action of the wool, so as to allow of its penetrating into the interior of the fiber before it is decomposed and fixed, and of the dissociation and absorption taking place simultaneously, without the intermediate formation of a precipitate in the liquor, which might be attracted and mechanically fixed by the wool.

"Taken as a whole, the salts of oxalic and tartaric acid fulfill these conditions best—a fact that reminds us of the property of the non-volatile organic acids to impede the precipitation of aluminum hydroxides by alkalies or other agents. On the other hand, the basic aluminum sulphates are entirely unsuitable for the mordanting of wool, because they dissociate before they are taken up by this fiber.

"Liechti and Schwitzer have compared *the action of sulphate, oxalate, and tartrate of aluminum in mordanting.* They prepared solutions of oxalate $Al_2(C_2O_4)_3$, and of aluminum tartrate, $Al_2(C_4H_4O_6)_3$, by dissolving two equivalents of aluminum hydroxide, $Al(OH)_3$, in three equivalents of oxalic and tartaric acid, respectively. If wool is boiled in a solution of *normal aluminum sulphate* the bath becomes exhausted if less than 5 percent sulphate (of the weight of the wool) is used. Larger amounts leave increasing proportions in the liquor. The mordanting baths become turbid on boiling by separating an insoluble aluminum salt. A part of the precipitate thus formed becomes mechanically fixed, and is removed on washing, the wash waters being turbid; a part remains in the mordanting liquor. The wool which has been mordanted gives an acid wash water on treatment with boiling water—thus proving that the aluminum sulphate has been decomposed, and that not merely alumina but free acid has been extracted from the mordanting bath. If *sulphuric acid is added to the mordanting bath,* the decomposition of the mordant is less rapid, and it is better fixed than when the normal sulphate is used alone. Comparatively large quantities of sulphuric acid are necessary—more than three equivalents H_2SO_4 of the sulphate, $Al_2(SO_4)_3$, and the effect of the acid decreases with an increasing dilution of the bath.

"*Alum* is a somewhat less efficient mordant than aluminum sulphate; this is evidently due to the dissociating effect which is exerted by the alkaline sulphates present in the former salt.

"*Normal aluminum oxalate,* $Al_2(C_2O_4)_3$, is almost completely taken up from the mordanting bath. A smaller amount of precipitate remains in the liquor, and less can be removed from the wool than in the case of mordanting with the normal sulphate. The wool, on treatment with boiling water, gives, in this case also, an acid wash water.

"*Normal aluminum tartrate*, $Al_2(C_4H_4O_6)_3$, if used as the wool mordant, leaves scarcely any precipitate in the bath, and does not give up any to the wash water. On treatment with hot water, the wool imparts also to the latter an acid reaction. Boiling water does not remove the mordant proper. Wool which had been boiled out several times with distilled water after mordanting, gave, on dyeing with alizarine, more brilliant and fuller colors than wool which had been simply rinsed in water. The normal tartrate can be replaced, with excellent results, by a mixture of one equivalent of aluminum sulphate and three equivalents of tartar (acid potassium tartrate)

$$Al_2(SO_4)_3 + 3KC_4H_5O_6 = Al_2(C_4H_4O_6)_3 + 3KHSO_4.$$

In this case, as shown by the equation, a mixture of normal aluminum tartrate and acid potassium sulphate is formed. If the normal tartrate is prepared by double decomposition, *e. g.*, with normal potassium-sodium tartrate (Rochelle salt), as in the following equation:

$$2Al_2(SO_4)_3 + 6KNaC_4H_4O_6 = 2Al_2(C_4H_4O_6)_3 + 3K_2SO_4 + 3Na_2SO_4,$$

the results obtained are not as good as those with the pure tartrate or with the mixture produced with tartar. These facts lead to the conclusion that the tartrate is similar to other aluminum salts, and is more rapidly dissociated in the presence of alkaline sulphates than in the pure state; and that in the case of a mixture of aluminum sulphate and tartrate being used, the acid sulphate prevents a premature dissociation.

"An examination of the spent mordants and dye-baths shows that the mordanting is most perfect in the case of the tartrate, the whole of the alumina being fixed in a permanent manner. It appears that not only the hydroxides but also true basic aluminum salts are deposited by the mordanting processes in the fiber, as on dyeing the well-washed wool with alizarine, the spent dye-liquors invariably show an acid reaction. These theoretical considerations and experiments are in perfect harmony with practical experience.

"Basic aluminum sulphates are not used as wool mordants, neither are the acetates nor sulphate-acetates, as they dissociate too rapidly and give poor results. By depositing too much of the mordant on the surface, they make the wool harsh and give rise to uneven dyeing and rubbing. Thiocyanate of aluminum, which is not as sensitive as the acetates, is a very good wool mordant; but its general employment is prevented by its high price.

"The aluminum mordant *par excellence* for wool is aluminum sulphate, either alone or in conjunction with acids or acid salts. In some cases the sulphate is used without any additions. Most generally, however, a mixture of the sulphate with the tartar substitutes is required to obtain full and brilliant colors which do not rub off. These tartar substitutes are sodium bisulphate or oxalates, or they consist of tartar which has been prepared with sufficient sulphuric acid to convert all of the potassium into potassium sulphate. From the foregoing it appears that none of these 'substitutes' can replace the tartar completely, because the action of the latter depends on the formation of *aluminum tartrate by double decomposition*. They have, of course, some effect, as has also sulphuric acid. For a full shade about 6 to 8 percent aluminum sulphate and 5 to 7 percent tartar (of the weight of the wool) are necessary. The quantity of tartar may be reduced to about half this amount, or it may be partly or even wholly replaced by sulphuric, hydrochloric, oxalic acid, bisulphate or sodium, etc., with very good, though not equally fine, results. About 4 percent of sulphuric acid (of the weight of the wool) is used, if the amount of water does not exceed 50 to 60 times the weight of the wool; otherwise more acid must be applied. When sulphuric acid has been used in mordanting, it is often beneficial to add about 5 percent sodium acetate to the ultimate dye-bath to neutralize the mineral acid which always remains in the wool fiber (and which otherwise would be converted into potassium sulphate if tartar had been employed). The mordanting bath is prepared with the necessary quantities of aluminum sulphate and tartar (or its substitutes) and the wool is entered at a low temperature. During one to one and a half hours the bath is heated gradually to boiling and boiled for half an hour more. When the bath has cooled down the wool is taken out and thoroughly washed in water; boiling out with water is beneficial. It has been shown that washing is absolutely necessary to remove all loosely adhering mordants and to prevent rubbing of the ultimate color. The washing, moreover, removes some of the acid, which is absorbed by wool, and would be injurious in dyeing. The washed wool is ready for dyeing; it should not be allowed to dry, as it is then very difficult to wet out again."

In the chapter on mordants Herzfeld[1] says: "It is well known that wool has acid and basic properties; the latter [?] enables it, when boiled in a bath of aluminum sulphate, to decompose the salt and to precipitate basic salt or alumina on the fiber. This takes place very rapidly and the precipitate is not properly adsorbed by the fiber. The precipitation takes place more slowly and more regularly if organic acids are present, wherefore oxalic acid, lactic acid, tartar, or something similar, is always added when mordanting wool. These counterbalance the effect of the mineral acid set free in the process."

Beech[2] discusses the mordanting of wool. "The mordanting method is one of the most generally useful. It consists in first causing a combination of the metal with the wool fiber. This is carried out by boiling the wool in a solution of the metal, such as bichromate of potash, chrome alum or chrome fluoride, when chrome is to be used as a mordant, with alum or sulphate of alumina when alumina is required to be deposited on the fiber, and with copperas when iron

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[1] "Das Färben und Bleichen der Textilfasern," 58 (1900).

[2] "The Principles and Practice of Wool Dyeing," 71 (1902).

is to be the mordant. It is best to add a little oxalic acid, cream of tartar or tartaric acid to the mordanting bath, which addition helps in the decomposition of the metallic salt by the wool fiber, and the deposition of the metallic oxide on the wool. With bichromate of potash, sulphuric acid is often used, much depending upon the character of the mordant required. Some dye-stuffs, such as logwood for blacks, work best when the wool is mordanted with chromic acid, which is effected when sulphuric acid is the assistant mordant. Other dye-stuffs, such as fustic, Persian berries, and alizarine yellow, are best dyed on a basic chrome mordant, which is effected when tartar or oxalic acid is the assistant mordant used, or when some other form of chrome compound than bichromate is employed.

"The actual mordanting is done by boiling the wool in a bath of the mordant, the quantity of which should be varied according to the particular mordant that is being employed and to the quantity of dye-stuffs which is to be used. It is obvious that for fixing a deeper shade of, say, alizarine on the wool, a larger quantity of mordant will be required than to fix a pale shade; sometimes this point is overlooked and the same amount of mordant employed for pale or deep shades. The best plan of carrying out the mordanting is to enter the wool in the cold bath or at a hand heat, and then raise to the boil and continue the boiling for one hour; of course the goods should be kept turned over during the process to facilitate the even mordanting of the wool. A great deal of the success of dyeing with the dye-stuffs now under consideration depends upon the efficiency with which the mordanting has been carried out. If this is at all unevenly done, then no amount of care in the succeeding dyeing process will lead to the development of an even dyeing. After the mordanting is finished, the goods should be rinsed with water, but it is not necessary to dry them."

These results are exactly what one can predict according to the adsorption theory of mordanting because the theory was designed with that in mind. The more basic the solution the greater the hydrolysis and the more rapid the precipitation. Consequently so-called basic solutions cannot be used with wool. While aluminum sulphate does not hydrolyze so much as the aluminum salt of a weaker acid, the coagulating effect of sulphate causes the alumina to precipitate more rapidly and in a less satisfactory form. Addition of sodium sulphate increases the concentration of sulphate and makes matters worse. Addition of sulphuric acid tends to work both ways. The increase in acidity cuts down the hydrolysis and tends to prevent precipitation of alumina. Increase in the sulphate concentration tends to increase the rate of coagulation. The effect due to the increasing acidity is the more important one and consequently an aluminum sulphate solution, acidified with sulphuric acid, works better than an aluminum sulphate solution which has not been acidified at all, and very much better than an aluminum sulphate solution to which sodium sulphate has been added. If we acidify with an organic acid the two factors work together, because the organic acid acts as a peptonizing agent on alumina instead of pectizing it as sulphates do. Those organic acids are the most satisfactory which are the most effective in preventing rapid coagulation of the alumina. It is worth while to compare the three quoted statements in regard to this point. Knecht, Rawson and Loewenthal say that the aluminum salts of oxalic and tartaric acids possess a certain resistance to the dissociating action of wool, which is not true because these salts hydrolyze considerably more than the sulphate. Beech says that addition of oxalic acid, cream of tartar or tartaric acid to the mordanting bath helps in the decomposition of the wool salt by the wool fiber, which is not true, because increasing the acidity cuts down the hydrolysis. Herzfeld is perfectly right in saying that precipitation takes place more slowly and more regularly if organic acids are present; but this is not especially helpful because he does not make any attempt at an explanation why organic acids should have such an effect. Instead of this jumble of contradictory explanations, the adsorption theory straightens the whole matter out; what happens is just what one would expect from a knowledge of the chemistry of the reacting substances. What has been said about oxalic and tartaric acids applies with suitable modifications to formic acid[1] and to lactic acid.[2]

Having taken up the case of alumina mordant in such detail, it hardly seems necessary to discuss the other metallic mordants now. The same principles are involved and the slight differences in behavior do not seem to present anything new.[3] The difference between the mordanting of wool and of cotton is what one would expect from the lesser adsorbing power of cotton. With cotton the solutions must be more basic and the use of a fixing agent for the mordant is more important.

There is one more point about alumina mordants which I wish to establish before bringing this first paper on mordants to a close. The brilliancy of a mordanted color will depend very largely on the transparency of the mordant. The most brilliant colors are obtained with a tin mordant[4] apparently because this mordant is the most transparent. Cajar[5] finds that when soda is added to a cold aluminum sulphate solution, the precipitate is white and has a distinct covering power. If the precipitate is heated or if soda is added to a hot solution the precipitate is more transparent. This is in line with the general fact that precipitates are less amorphous and more crystalline the higher the temperature of precipitation[6] provided the other conditions are kept the same. Raising the temperature of the mordanting bath therefore gives a more transparent mordant. It also helps to fix the mordant better on the fiber; but that is a point which can be postponed until I take up the whole question of fastness of dyes.

Since we get a more transparent mordant by raising the

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[1] Boehringer and Soehne: Zeit. Farbenindustrie, 9, 237, 353 (1910).

[2] Schwalbe: Zeit. Kolloidchemie, 5, 129 (1909).

[3] Liechti and Suida: Jour. Soc. Chem. Ind., 5, 526 (1886).

[4] Herzfeld: "Das Färben und Bleichen der Textilfasern," 73 (1900); Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 2nd Ed., 276 (1910).

[5] Zeit. angew. Chem., 24, 793 (1911).

[6] Cf. Owens: Jour. Phys. Chem., 18, 461 (1914).

temperature of the bath, the question arises whether it might not be better to raise the temperature still more if possible or to keep the bath longer at the boil. This might be desirable if transparency were the only thing to be considered. It so happens that another factor comes in. At high temperatures the alumina becomes denser, presumably losing water, and loses its mordanting powers.[1] This fact is recognized by practical dyers[2] "Goods which have been impregnated with the acetates and sulphate-acetates must not be dried at high temperatures, since these compounds are most readily dissociated on the fiber by heat, when acetic acid escapes and the base remains on the fiber in a form which renders it less capable of combining with the coloring matter in the subsequent dye-bath; poor and irregular colors would thus result. This fact may be due to the generation of aluminum oxide instead of the hydroxide, as shown by either of the following equations:

$$2Al(CH_3CO_2)_3 + 3H_2O = Al_2O_3 + 6CH_3CO_2H$$
$$2Al(CH_3CO_2)_2OH + H_2O = Al_2O_3 + 4CH_3CO_2H$$

Another explanation is that a basic acetate or a less hydrated aluminum hydroxide is formed, neither of which forms color lakes. Mordants that have been spoiled by overheating are said to have been burned."

The general results of this paper are as follows:

1. A mordant is a substance which is adsorbed strongly by the fiber and which adsorbs the dye strongly.

2. There is no evidence that any definite compounds are formed when the metallic mordants are taken up by wool, silk or cotton.

3. The difference between the behavior of wool and of cotton is merely one of degree.

4. Aluminum salts hydrolyze more or less completely

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[1] Cf. Crum: Jour. Chem. Soc., 6, 227 (1854).

[2] Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 2nd Ed., 235 (1910).

when dissolved in water, the change being more rapid at high temperatures.

5. When aluminum salts hydrolyze, or when small amounts of sodium carbonate are added to the solution, colloidal alumina is one of the reaction products.

6. With aluminum acetate the hydrolysis is so rapid that no considerable amount of normal acetate is formed when equivalent solutions of aluminum sulphate and lead acetate are mixed.

7. Coagulated alumina causes so-called aluminum acetate to hydrolyze further and hydrous ferric oxide has a similar effect on ferric chloride.

8. The fact that aluminum chloride will hold in solution more alumina than it can carry into solution is proof that we are not dealing with a definite basic salt.

9. The solutions used by Liechti and Suida did not contain the basic salts that were supposed to be there.

10. Since Liechti and Suida did not approximate equilibrium conditions in their mordanting experiments, the results are too uncertain to have any value.

11. The metallic mordants are hydrous oxides and not basic salts.

12. The rate of coagulation is more important than the degree of hydrolysis.

13. Normal and so-called basic aluminum sulphates coagulate too readily to be satisfactory with wool.

14. Addition of sodium sulphate increases the rapidity of coagulation from normal or basic aluminum sulphate solutions.

15. Addition of sulphuric acid retards the coagulation of alumina; addition of organic acids is still more helpful.

16. The upholders of the chemical theory of dyeing give diametrically opposed explanations for the action of organic acid.

17. More transparent mordants are obtained from hot solutions than from cold solutions; but they have less mordanting power.

18. Alumina mordant may be taken as a typical basic mordant. What is true of this is true of the other mordants with slight and obvious changes.

19. The differences in the mordanting of wool and of cotton are what would be expected from the lesser adsorbing power of cotton.

Cornell University

THE RATE OF DISSOCIATION OF NITROGEN PEROXIDE

BY W. L. ARGO

The relation between the pressure, temperature and density of nitrogen peroxide is satisfactorily expressed by the statement that there is equilibrium between two gases with formulae N_2O_4 and NO_2.[1] Up to the present, no experiments have been made with the object of ascertaining whether any appreciable time is required for establishing equilibrium between these two gases, after an alteration of pressure. The purpose of the present paper is to determine whether in very rapid changes of pressure there is any evidence of "lag" in the reaction.

In his experiments on the rates of reaction of gases, van't Hoff[2] found that in many cases the walls of the vessel hastened the reaction. To eliminate this factor, and at the same time to obtain the necessary rapidity in the pressure changes, the oscillations of stationary sound waves have been made use of in this research.

If the change of dissociation is very rapid there will be equilibrium between the nitrogen tetroxide and dioxide, according to the equation $N_2O_4 \rightleftarrows 2NO_2$, at every instant during the oscillations of the sound waves, and the local density of the gas at each moment will correspond to what would be found by ordinary density measurements for the local pressure and temperature.

If, on the other hand, the rate of reaction is so small that no appreciable changes in dissociation occur, the density at every moment will be that calculated by the gas law $pV = nRT$, when n is constant.

If the velocity of sound in nitrogen peroxide can be calculated with sufficient accuracy for each of these limiting assumptions, it will be possible, by measurement of sound velocity

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[1] Gibbs: Trans. Conn. Acad., 3, 240 (1878).

[2] Van't Hoff-Cohen: Studien zur chemischen Dynamik, p. 45 (1896).

in the gas, to decide whether the rate of dissociation corresponds to either one of these limiting cases or has some intermediate value.

Calculation of $d\rho/dp$

Symbols used:

T = absolute temperature.
p = pressure of nitrogen peroxide in mm mercury.
p_1 = pressure of air in mm mercury.
V = volume in cc of 92.08 grams nitrogen peroxide at p.
V_1 = volume in cc of 28.97 grams air at p_1.
d = density of nitrogen peroxide compared with air, at T and p.
$\rho = \frac{92.08}{V}$ (density of nitrogen peroxide, in grams per cc).
$\rho_1 = \frac{28.97}{V_1}$ (density of air in grams per cc).
R = 62340.
$\alpha = 92.08/28.97d - 1$ ("degree of dissociation").
c_v' = sp. heat per formula weight, at constant volume, of NO_2.
c'' = sp. heat per formula weight, at constant volume, of N_2O_4.
$c_v = \frac{(1 - \alpha)c_v'' + 2\alpha c_v'}{1 + \alpha}$.
κ_1 = 1.405 (Ratio of specific heats at constant pressure and constant volume for air).
K = dissociation constant of nitrogen peroxide, defined by $\frac{4\alpha^2}{V(1 - \alpha)} = K$.
h = heat given out, in cal., when N_2O_4 changes to $2NO_2$ at constant volume.
λ = wave length in cm of stationary sound waves in nitrogen peroxide.
λ_1 = wave lengths in cm of stationary sound waves in air.
ν = no. of vibrations per second of rod forming sound waves.

Calculation of $\frac{d\rho}{dp}$ *from wave lengths.* From the formulae for the velocity of sound.[1]

$$\frac{d\rho}{dp} = \frac{\text{const.}}{\lambda^2\nu^2};\quad \frac{d\rho_1}{dp_1} = \frac{\text{const.}}{\lambda_1^2\nu^2},$$

$$\frac{d\rho}{dp} = \frac{\lambda_1^2\rho_1}{\lambda_1^2 p\kappa_1}. \qquad (1)$$

This gives an experimental method for determining $\frac{d\rho}{dp}$

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[1] Clausius: Mech. Wärmetheorie, p. 52 (1876).

for nitrogen peroxide from measurements of wave length in it and in air, for the same note.

Calculation of hypothetical $\frac{d\rho}{dp}$. The value of $\frac{d\rho}{dp}$ may be calculated under the two assumptions made above:

Assumption A.—That the dissociation is so rapid that chemical equilibrium exists at every moment.

Assumption B.—That the dissociation is so slow that no chemical reaction takes place during the changes due to the sound waves.

The values under Assumptions *A* and *B* will be indicated by $\left(\frac{d\rho}{dp}\right)_A$ and $\left(\frac{d\rho}{dp}\right)_B$, respectively. These will be compared with the experimental value $\left(\frac{d\rho}{dp}\right)_{\text{exp.}}$ given by equation (1).

For a small adiabatic change of the nitrogen peroxide

$$0 = -h\left(\frac{\partial\alpha}{\partial V}\right)_T dV + \frac{1.359}{42660}p\,dV - h\left(\frac{\partial\alpha}{\partial T}\right)_v dT + (1-\alpha)c''_v dT$$
$$+ 2\alpha c'_v dT$$

$$\therefore \frac{dV}{dT} = \frac{h\left(\frac{\partial\alpha}{\partial T}\right)_v - (1-\alpha)c''_v - 2\alpha c'_v}{\frac{1.359}{42660}p - h\left(\frac{\partial\alpha}{\partial V}\right)_T}. \tag{2}$$

Also

$$(1+\alpha)RT = pV. \tag{3}$$

From (2) and (3), and noting that $\frac{d\rho}{dp} = -\frac{\rho}{V}\frac{dV}{dp}$

$$\frac{d\rho}{dp} = -\frac{\rho}{\frac{R\left\{T\left(\frac{\partial\alpha}{\partial T}\right)_v + 1 + \alpha\right\}\left\{\frac{1.359}{42660}p - h\left(\frac{\partial\alpha}{\partial V}\right)_T\right\}}{h\left(\frac{\partial\alpha}{\partial T}\right)_v - (1-\alpha)c''_v - 2\alpha c'} + RT\left(\frac{\partial\alpha}{\partial V}\right)_T - p}. \tag{4}$$

Under *Assumption A*, since $K = \frac{4\alpha^2}{V(1-\alpha)}$,

$$\left(\frac{\partial\alpha}{\partial V}\right)_T = \frac{K(1-\alpha)^2}{4(2-\alpha)} = \frac{\alpha^2(1-\alpha)p}{(2-\alpha)RT}.$$

And since from van't Hoff's equation, $\frac{dln\mathrm{K}}{d\mathrm{T}} = -\frac{h}{1.985\mathrm{T}^2}$,

$$\left(\frac{\partial\alpha}{\partial\mathrm{T}}\right)_v = -\frac{h\alpha(1-\alpha)}{1.985\mathrm{T}^2(2-\alpha)}.$$

Equation (4) now becomes by substitution

$$\left(\frac{d\rho}{dp}\right)_\mathrm{A} = \frac{\frac{\rho}{p}}{\frac{\left\{-\frac{h\mathrm{M}}{1.985\mathrm{T}} + (1+\alpha)\right\}\left\{1.985 - \frac{h\alpha\mathrm{M}}{\mathrm{T}}\right\}}{\frac{h^2\mathrm{M}}{1.985\mathrm{T}^2} + (1-\alpha)c''_v + 2\alpha c'_v} - \alpha\mathrm{M} + 1} \qquad (5)$$

in which $\mathrm{M} = \frac{\alpha(1-\alpha)}{2-\alpha}$ and α has the value calculated from ordinary density measurements.

Under *Assumption B* $\left(\frac{\partial\alpha}{\partial\mathrm{V}}\right)_\mathrm{T} = 0$ and $\left(\frac{\partial\alpha}{\partial\mathrm{T}}\right)_\mathrm{V} = 0$, and equation (4) becomes

$$\left(\frac{d\rho}{dp}\right)_\mathrm{B} = -\frac{\rho}{\frac{\mathrm{R}(1+\alpha)\frac{1.359p}{42660}}{-(1-\alpha)c''_v - 2\alpha c'_v} - p} = \frac{c_v}{c_v + 1.985}\cdot\frac{\rho}{p}. \qquad (6)$$

corresponding to Laplace's formula for an ordinary gas.

Data Used.—For h the value —12900 cal., calculated by van't Hoff,[1] has been used. The values of α were calculated from the density ρ, by equation (3); ρ and p were found directly by E. and U. Natanson in their determinations of sound wave length. In my experiments the weight, volume and temperature were determined and the pressure was found by Gibbs' equation[2]

$$\log_{10}\frac{(3.178-d)^2\mathrm{P}}{2(d-1.589)} = 9.47056 - \frac{3118.6}{\mathrm{T}}$$

in which P is the pressure in atmospheres.

The only data about which there is much uncertainty are the values of c'_v and c''_v. From Berthelot and Ogier's[3]

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[1] Van't Hoff-Cohen: Studien zur chem. Dynamik, p. 158 (1896).

[2] Gibbs: Trans. Conn. Acad., 3, 239 (1878).

[3] Ann. Chim. Phys., [5] 30, 382 (1883).

determinations of the total heat given out on cooling nitrogen peroxide through various intervals of temperature, and taking the heat of dissociation as —(13132 + 2T) cal., Schreber[1] has calculated the values of c'_v and c''_v on the assumption that $c''_v = 2c'_v$. He gives the values 12.85 and 6.43. His calculation, however, contains the erroneous assumption that the heat required to raise the temperature of 92.08 grams of nitrogen peroxide through 1° at constant volume (C_v) is equal to the corresponding value for constant pressure 14.85 cal., (C_p), less 1.985 (instead of $(1 + \alpha)1.985$). Moreover, Schreber's number 14.85 was obtained by averaging the values found for various intervals of temperature ranging from about 290° - 28° to 150° - 28° on the wrong assumption that C_p is independent of the temperature. The specific heat at constant pressure for 92.08 grams must increase with increasing dissociation according to the equation $C_p = C_v + 1.985(1 + \alpha)$. Unfortunately the experimental data on which these values are based are not sufficiently concordant to warrant a strict recalculation. A rough estimate, however, was made as follows:

By taking intervals of temperature θ (about 25° each) from 290° to 28°, and calculating the values of $\theta\{(1 - \alpha)c''_p + 2\alpha c'_p\}$ for the averages of the value of α at the upper and lower ends of each interval, and summing these values over intervals corresponding to Berthelot and Ogier's experiments, a set of numbers is obtained whose average is 14.85 when c''_p is taken as 13.4 and c'_p as 7.7.[2] This gives $c''_v = 11.4$ and $c''_v = 5.7$.

The value $c'_v = 5.7$ is low compared with those of other gases of similar formulae, as shown by the following table:

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[1] Zeit. phys. Chem., 24, 651 (1897).

[2] These values were found after a few approximations. c''_v is assumed equal to $2c'_v$. This assumption is justified to a certain extent by the fact that the relation between density of nitrogen peroxide and temperature is closely represented by an equation of Gibbs' in which this assumption is implied. (See Trans. Conn. Acad., 3, 244 (1878).)

CO_2	7.55
N_2O	7.95
H_2O	6.65
SO_2	7.88
H_2S	6.27
CS_2	9.93
Average,	7.70

If in these calculations the value —12900 cal., calculated by van't Hoff from Deville and Troost's measurements is used for the heat of dissociation instead of —13132 cal., calculated by Schreber from Natanson's experiments, the values for c''_v and c'_v would come out about 12 percent greater, say 12.8 and 6.4. Van't Hoff[1] mentions the value 16.86 for 92 grams of nitrogen peroxide "at high temperatures where decomposition can be neglected," but does not say how he obtained it. This would give 16.86/2 — 1.985 = 6.45 for c''_v. Because of this agreement with van't Hoff's value, and the higher values for other gases, the values

$$c''_v = 12.8 \text{ and } c'_v = 6.4$$

have been used in the calculations. Fortunately the effect of errors in the specific heats on the values $\left(\frac{d\rho}{dp}\right)_A$ and $\left(\frac{d\rho}{dp}\right)_B$ are relatively small. (See p. 444.)

Comparison of Calculated and Observed Values of $\left(\frac{d\rho}{dp}\right)$

The following table shows the calculated values of $\left(\frac{d\rho}{dp}\right)_A$, and $\left(\frac{d\rho}{dp}\right)_B$, and the values of $\left(\frac{d\rho}{dp}\right)_{exp.}$ obtained from four sets of the sound wave measurements of E. and U. Natanson:[2]

t	p mm	d (measured)	λ_1 mm	λ mm	$\left(\frac{d\rho}{dp}\right)_A \times 10^6$	$\left(\frac{d\rho}{dp}\right)_B \times 10^6$	$\left(\frac{d\rho}{dp}\right)_{exp.} \times 10^6$
21.72° C	230.59	2.486	42.09	23.64	3.659	3.275	3.558
21.25	367.08	2.599	42.05	23.08	3.833	3.452	3.733
21.81	617.63	2.709	41.80	22.27	3.987	3.619	3.953
19.96	640.76	2.762	41.98	22.19	4.092	3.718	4.042

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[1] Van't Hoff-Cohen: Studien zur chem. Dynamik, p. 158 (1896).

[2] Wied Ann., 24, 454 (1885).

The experimental values $\left(\frac{d\rho}{dp}\right)_{\text{exp.}}$ agree very closely with those for $\left(\frac{d\rho}{dp}\right)_{\text{A}}$, the greatest deviation being 2.8 percent and the least 0.9 percent. On the other hand, the experimental values differ from $\left(\frac{d\rho}{dp}\right)_{\text{B}}$ by from 8.5 percent to 7.5 percent.

The Effect of Errors in Data

The following table shows the percent effect on the values at the heads of the columns caused by a one percent increase in the data shown in the first column:

	$\left(\frac{d\rho}{dp}\right)_{\text{A}}$	$\left(\frac{d\rho}{dp}\right)_{\text{B}}$	$\left(\frac{d\rho}{dp}\right)_{\text{exp.}}$
λ_1	0	0	+2
λ	0	0	—2
α	+1.04 to +0.96	+1.15 to +1.17	0
c_v	+0.013 to +0.010	+0.15 to +0.17	0
$-h$	+0.05 to +0.09	0	0

Thus, to bring the values $\left(\frac{d\rho}{dp}\right)_{\text{exp.}}$ down to the values $\left(\frac{d\rho}{dp}\right)_{\text{B}}$ there would have to be consistent errors of about +4 percent in λ, or —4 percent in λ_1 (or +2 percent in λ *and* —2 percent in λ_1). Chance errors in the measurement of wave length are much less than this (see values, page 449), and it is quite improbable that methodical errors would have opposite signs in λ and λ_1.

To bring the values $\left(\frac{d\rho}{dp}\right)_{\text{B}}$ up to the value $\left(\frac{d\rho}{dp}\right)_{\text{exp.}}$ an error of about +7 percent would be necessary in *d*, or an error of about +50 percent in c_v. Errors of these magnitudes are practically impossible in *d*, and very unlikely even in the case of the doubtful c_v.

The results of the above comparison may be taken therefore as conclusive evidence that *Assumption B* is not in accordance with the facts.

It may be noted in connection with this conclusion that it is clearly impracticable to use sound velocity as a means of measuring the ratio $\frac{C_p}{C_v}$ for nitrogen peroxide.

New Experiments

Natanson's determinations involved the use of a mercury manometer and stop-cocks. The stop-cock lubricant is readily attacked by the nitrogen peroxide, and as a result water vapor in slight traces may have reached the gas and catalysed the reaction. In order to check the above conclusion with a carefully dried gas and, at the same time, to investigate the effect of water vapor, added in known quantity, the following experiments were carried out.

The apparatus finally designed had neither stop-cocks nor manometer. The stop-cocks were eliminated because it was found that even metaphosphoric acid used as lubricant allowed leaks. As the use of a manometer would require stop-cocks to protect the mercury from the peroxide, the pressure of the gas was calculated from measurements of its volume and weight by the use of the Gibbs' equation (see page 441).

The sound-producing apparatus was somewhat different from the Natanson type. The sounding tube AB, 120 cm long and 1.0 cm cross section, with a flattened bulb at each end, is clamped at its middle, C. It is sealed into the gas chamber DF at D, so that DB is 20 cm long. As this is equivalent to a second clamp at D the sounding tube is damped at

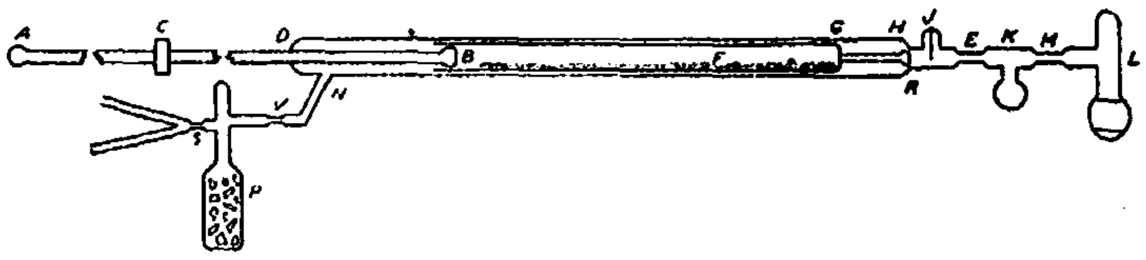

Fig. 1

$^1/_2$ and $^1/_4$ its length. The gas chamber in this way is theoretically stationary, whereas in the Natanson type it formed part of the vibrating system. The apparatus is thus less fragile and the dust heaps are less irregular than when they are formed on a vibrating surface. The adjustment of length of the gas column is made by means of an inner tube F, supported by platinum loops sealed into its walls. It can be adjusted by tapping the end of the gas chamber. The loops fitted tightly enough to prevent the tube from sliding when the apparatus was held vertically. The powder for forming the dust heaps, precipitated silica, was placed in this inner tube.

At G a glass rod GH was sealed into the flat end of the inner tube. Its length was such that when the tube was moved back sufficiently, a capillary tube, sealed in at J, was broken. This capillary contained about 0.001 gram of water. The bulb K, of about 6 cc capacity, in which the nitrogen peroxide was to be finally condensed by liquid air, opened into the nitrogen peroxide reservoir L and the gas chamber through constrictions E and M. The side tube N opened into a glass bulb P containing cocoanut charcoal which was in communication with an air pump and a McLeod gauge.

The nitrogen peroxide was prepared from pulverized lead nitrate dried for an hour at about 120° C. This was mixed with dry sand to prevent caking, and was decomposed in a combustion tube through which passed a strong current of dry oxygen. The nitrogen peroxide was condensed in the reservoir L, of about 15 cc capacity, containing phosphorus pentoxide. The reservoir was then sealed off until ready for use. The nitrogen peroxide remained in contact with the phosphorus pentoxide for one week before it was used in the experiment.

The preparatory operations were as follows: The apparatus from D to K was enclosed in a heating oven. The nitrogen peroxide reservoir was immersed in liquid air, opened, and sealed to the apparatus at M. (The blowing was done through a phosphorus pentoxide tube to prevent access of moisture.) When the air-pump was started, the nitrogen peroxide was heated to its melting point and then re-frozen slowly to prevent the lodging of air bubbles in the interstices of the frozen mass. The bulb was then kept immersed in liquid air.

The apparatus from D to R was heated to 195° C to remove the adsorbed water from the powder and from the walls of the vessel. As previous experiments had shown that at this temperature the water in the capillary etched and cracked the glass the part RM was heated only to 150° C. The bulb P was also heated to 200° C. When, after about three hours, the system had been exhausted to a pressure of 0.02 mm, the gauge and pump were sealed off at S. The bulb P was then immersed in liquid air to produce as complete a vacuum as possible. After six hours the bulb was sealed off at V and the reservoir L was removed from the liquid air. After allowing the apparatus to reach room temperature, about 20° C, and making certain that no nitrogen peroxide had condensed in the gas chamber, the reservoir L was sealed off at M.

In the adjustment of the apparatus to form stationary sound waves, the sounding tube, clamped at D, was rubbed between C and D with ether-moistened cotton wool. The length of the gas column in the inner tube BG was then altered by gentle tapping until well-defined heaps were formed.

After this preliminary adjustment the gas cylinder was placed in a thermostat at 22° C. For easy removal of the apparatus this consisted of a water tank, kept at 22° C ± 0.05, through which a cylinder about 8 cm in diameter ran longitudinally. When the apparatus had been supported by brass clips in this cylinder the openings were closed with loosely packed cotton wool. The temperature of the air-bath so formed reached that of the water tank about an hour after the apparatus had been inserted, and remained at 22° C ± 0.1 throughout an experiment.

To secure the necessary rigidity the clamp for damping the sounding tube at the point C was imbedded in a heavy concrete block. A layer of cork fastened to the glass with adhesive tape and fish glue prevented the tube from slipping through the clamp.

When the temperature of the air-bath had become 33° C the sounding tube was clamped at C and set into vibration as before. Then the apparatus was removed from the thermostat and the dust-heaps were measured to 0.5 mm. The readings were averaged by the method proposed by Kundt.[1] Repetitions of this procedure gave a series of readings as checks on the measurement.

The wave length in air, λ_1, was obtained at the same time by inserting the end A of the sounding tube into a glass tube about 3 cm diameter and 50 cm long, containing precipitated silica. The temperature of the air was determined by two thermometers at either end of the tube and the dust heaps were measured as in the gas cylinder.

When a sufficient number of readings had been made, the capillary containing the water was broken. To insure distribution of the moisture throughout the nitrogen peroxide the gas cylinder was heated and cooled several times and the inner tube BG moved backwards and forwards. The gas cylinder was then left in the thermostat for twenty-four hours. With the nitrogen peroxide now definitely known to contain water vapor another wave-length measurement was made.

To determine the weight of nitrogen peroxide in the gas cylinder, the bulb K was immersed in liquid air until no color could be distinguished by looking longitudinally through RD. After the bulb was sealed off at E and dried, it was placed in a desiccator for half an hour and was then weighed. Both the bulb and a standardized solution of potassium permanganate were cooled in ice and then the top of the bulb was broken and held under the solution. In this way all the nitrogen peroxide was absorbed by the potassium permanganate. (No odor of the gas was distinguishable above the solution.) The permanganate reduced by the nitrous acid was determined by titrating with freshly standardized ferrous sulphate solution.

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[1] Pogg. Ann., 127, 497 (1866).

The weight of nitrogen peroxide in the bulb was thus determined.

The weight was also determined directly by weighing the dried bulb and broken tip. A satisfactory check between the two methods served to establish the purity of the nitrogen peroxide.

Finally the volume of the gas cylinder was determined by weighing it empty and filled with water.

The complete results of the experiments are given below.

Length of waves in nitrogen peroxide at 22 °C			Length of waves in air at 19.0 °C	
Expt. No.	Dry or moist	In cms.	Exp. No.	In cms.
E4	Dry	1.440	E1	2.659
E9	Dry	1.440	E3	2.669
E10	Dry	1.436		——
E12	Dry	1.455		Average, 2.664
E13	Dry	1.442		
E15	Dry	1.436		
		Average, 1.441		
E16	Moist	1.442[1]		

Weight of Nitrogen Peroxide in Bulb.

(a) By titration:

No. cc pot. permang. (0.2874*N*) = 202.75 cc.
No. cc ferrous sulphate (0.1686*N*) = 137.60 cc.
Net pot. permang. = 122.01 cc.
Weight nit. peroxide = 1.6129 gm.

(b) By direct weighing:

Wt. of bulb + nit. peroxide + 0.0012 gm. water = 7.4318 gm.
Wt. of opened bulb + pieces (empty) = 5.7976 gm.
Wt. of water = 0.0012 gm.
Wt. of nit. peroxide = 1.6330 gm.

The average value 1.623 grams was used in the calculation.

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[1] The sounding tube was accidentally broken while another "moist" measurement was in progress. As the dust heaps in E16 were well defined it was thought unnecessary to make further experiments.

Volume of Gas Chamber.

Wt. of tube + bulb empty = 480.5 gm.
Wt. of tube + bulb full of water at 19.5° C = 1036.0 gm.
Volume = 556.5 cc.

The values $\left(\frac{d\rho}{dp}\right)_A$, $\left(\frac{d\rho}{dp}\right)_B$ and $\left(\frac{d\rho}{dp}\right)_{exp.}$ were calculated as already explained.

t	d	p	$\left(\frac{d\rho}{dp}\right)_A \times 10^6$	$\left(\frac{d\rho}{dp}\right)_B \times 10^6$	$\left(\frac{d\rho}{dp}\right)_{exp.} \times 10^6$
22.0° C	2.722	679.9 mm	4.002	3.629	3.873

It is seen that the experimental value agrees with $\left(\frac{d\rho}{dp}\right)_A$ within 3 percent. This is probably within the limits of the experimental errors. On the other hand, it differs by more than 6 percent from the value $\left(\frac{d\rho}{dp}\right)_B$. This is in accord with the results calculated from Natanson's measurements. It can be concluded, therefore, that the rate of reaction even in the dry gas does not correspond to *Assumption B.*

Summary of Conclusions

1. The rate of reaction between nitrogen tetroxide and nitrogen dioxide is so great that there is no appreciable lag in the reaction during the rapid changes of pressure caused by stationary sound waves in nitrogen peroxide.

2. Conclusion 1 holds both for nitrogen peroxide dried over phosphorus pentoxide and for the gas containing 0.32 volume percent of water vapor.

3. It is impracticable to use measurements of sound velocity for determining $\frac{c_p}{c_v}$ for nitrogen peroxide.

This research was carried out at the suggestion and under the direction of Dr. F. B. Kenrick. The experimental work was completed at the University of California.

University of Toronto
University of California
January, 1914

NEW BOOKS

Physikalische Chemie der homogen und heterogenen Gasreaktionen. *By Karl Jellinek. 18 × 24 cm; pp. v + 844. Leipzig: S. Hirzel, 1913. Price: 32.50 marks.*—The main subdivisions are: statics of gas reactions; kinetics of gas reactions; electrochemistry of gas reactions; photochemistry of gas reactions. Under statics, or thermodynamics, of gas reactions the theoretical portion includes chapters on: the two laws of thermodynamics; statics of gas reactions treated by means of reversible cycles; statics of gas reactions treated by means of entropy and the deduced functions of free energy and thermodynamic potential; theory of heat radiation; relation between the quantum theory of heat radiation, the specific heats, the heats of reaction, and the Nernst heat theorem. The experimental part of the same subdivision includes: experimental data on heat radiation; determination of molecular oscillations by means of radiation; measurements of temperature; measurements of specific heats and heats of reaction; determination of gas equilibria. This first division is nearly ninety percent of the whole book, kinetics of gas reactions receiving thirty-five pages, electrochemistry of gas reactions forty-six pages and photochemistry of gas reactions twenty-two pages.

The author's general attitude is perhaps best shown by the fact that he calls Nernst's heat theorem the third law of thermodynamics. No reference is made to Johnston's criticism and the casual reader—assuming that such a man would read this book—would get the impression that everything was plain sailing and that there was no juggling with data. In spite of the hero worship, the author has written a very good book. He has given perhaps the clearest statement of Nernst's theorem; he has given an admirable sketch of the quantum theory in so far as it bears on the subject in hand, and everybody will be grateful to him for the data and literature references on gas equilibria.

For personal reasons the reviewer was interested in the following paragraph, p. 363: "We can divide substances into continuous radiators (highly heated solids and liquids, as well as gases which are not too dilute, all three acting as temperature radiators) and selective radiators, such as electrically excited dilute gases or vapors in Geissler tubes or arcs, chemically excited dilute gases in flames (luminescence), or heated dilute gases (thermal radiation). We picture a selective radiator (a dilute, luminescent gas) as a large mass of molecules in each of which there are one or more localized oscillators (vibrating electrons or ions) having one or more oscillation numbers. The vibrating electrons or ions can be excited only to vibrations of a definite period by collision with other electrons, ions, or molecules; and consequently emit electromagnetic waves of definite length discontinuously." *Wilder D. Bancroft*

Die Atome. *By Jean Perrin. Translated by A. Lottermoser. 16 × 22 cm; pp. v + 196. Leipzig: Theodor Steinkopff, 1914. Price: 5 marks.*—The French edition has already been reviewed (**17**, 563). We now have a German translation in a more convenient size. A quotation from the conclusions may not be amiss. After showing that the value, *N*, for the number of molecules in a gram molecular weight—the Avogadro number—falls between 60×10^{-22}

and 75 × 10^{-22}, when determined in thirteen different ways, the author goes on to say, p. 189: "We are filled with amazement at the close agreement among the numbers deduced from a study of such different phenomena. The probability of the actual existence of molecules becomes almost a certainty in view of the fact that the same method yields the same value no matter how the conditions of the experiment are varied, and in view of the fact that there is so little variation among the values obtained by so many methods. In spite of our firm belief in the existence of molecules, we must nevertheless be prepared to obtain an expression for the visible existence without having recourse to invisible elements. This can be done without trouble. We may eliminate N from the thirteen equations, which otherwise contain only directly measurable values, and obtain fundamental relations between basic phenomena which have hitherto seemed absolutely independent: the viscosity of gases, the Brownian movements, the blue of the sky, the radiation of the black body, and radioactivity.

"If we eliminate the Avogadro number from the equation for the radiation of a black body and from the equation for diffusion as due to the Brownian movements, for instance, we get a relation at once which enables us to predict the rate of diffusion in water at ordinary temperature of a sphere 0.001 mm. in diameter if we have measured the intensity of yellow light emitted by a furnace filled with molten iron. It is thus possible for a physicist who has studied the iron furnace to detect an error in the microscopical determinations of another man who was studying emulsions. This is possible without making any mention of molecules.

"We are not going to carry a mania for rigorous treatment so far as to make us avoid the use of molecular values in the mathematical expression of laws which we deduced by means of them. That would not be like removing the supporting stake when the plant had outgrown the need of it; but would be like cutting off the roots which nourish the plant and cause it to grow."

Wilder D. Bancroft

Qualitative Analyse vom Standpunkt der Ionenlehre. *By Wilhelm Böttger. Third edition. 17 × 24 cm; pp. vii + 565. Leipzig: Wilhelm Engelmann, 1913. Price: 11.20 marks, paper; 12.50 marks, bound.*—The second edition was reviewed five years ago (13, 177). The new edition differs from the previous one chiefly in that a section on microchemical methods has been added and that the portions dealing with reduction and oxidation have been rewritten. In the preface the author answers the criticism that the book is not suitable for an introductory course in qualitative analysis. He contends that it is better for the beginner to learn to find what he needs in a book which will also be helpful to him later rather than to use a little manual which contains just what he wants at the time but which will be worthless ever after. By this adroit move the author has certainly carried the war into Africa; but it is something of a question whether he can hold the ground which he has gained.

The rewritten chapter on oxidation and reduction shows how difficult it is to formulate anything rigorously even when one knows exactly how to deal with each special case. The author starts off, as everybody does, with the statement that reduction consists in the taking up of hydrogen or the loss of oxygen, oxidation being just the reverse of this. This goes to pieces in the reduction of mercuric chloride by copper or by stannous chloride, reactions not involving either hydrogen or oxygen. Ostwald tried to get round the difficulty by saying that we have reduction when we have a decrease in the number or valence of some cation and oxidation when there is an increase in the number or valence of some anion; but that would not meet a case of the type

$$H_2SO_3 + HClO = H_2SO_4 + HCl.$$

To meet this the author defines reduction as a decrease in the positive valence or an increase in the negative valence. This is perfectly correct provided one knows that the author means the valence of some element and not the valence of the ion. We have a precisely similar case in the Theorem of Le Chatelier which nobody has ever formulated rigorously, and yet which anybody will understand. It seems to the reviewer that it might often be well to dispense with definitions and to rely entirely on the illustrations, which one has to give anyway.
Wilder D. Bancroft

Les propriétés optiques des solutions. *By C. Chéneveau. 17 × 26 cm; pp. v + 240. Paris: Gauthier-Villars, 1913. Price: 10 francs.*—This book is really a new and enlarged edition of the author's doctor thesis. The subject is treated under the following headings: the theoretical laws of the refraction of solutions and of dissolved substances; the theoretical laws of the dispersion of solutions and of dissolved substances; deductions from the experimental study of aqueous solutions of inorganic substances; study of the refraction of solutions not entirely aqueous; experimental study of the dispersion of solutions of inorganic substances; experimental study of the refraction and dispersion of dissolved organic compounds; methods, apparatus and data. It is an ambitious programme; but there are practically no general results. The book is essentially a study of experimental facts. At the end of the book the author gives ten pages of literature references, for which everybody interested in this line of work will be grateful to him.
Wilder D. Bancroft

Zur Krise der Lichtäther-Hypothese. *By P. Ehrenfest. 14 × 22 cm; pp. 22. Berlin: Julius Springer, 1913. Price: 6 marks.*—This is an address delivered by the author when inaugurated as professor at the University of Leyden. Newton's emission theory of light was succeeded by the ether theory. Fresnel postulated a stationary ether and Stokes an ether which moved with moving substances. The development of Fresnel's views by Lorentz showed that the aberration of light from the stars, the velocity of light in running water, and the magnetic action of a rapidly rotating electrified body could be accounted for quantitatively on the basis of Fresnel's theory. On the other hand, the Michelson-Morley experiment seemed to favor Stokes' view. This difficulty was overcome when Lorentz showed in 1904 that the Michelson-Morley experiment gave a negative result, not because the result was really negative; but because the changes in the measuring instruments were equal to the result to be measured. While the Fresnel-Lorentz theory of a stationary ether seems to have triumphed over the theory of a moving ether, it has now to contend with the two different theories of Ritz and of Einstein, each of these theories postulating that there is no ether at all. The reviewer is not competent to say whether the author has or has not been strictly impartial in his presentation; but the address is certainly a model one from the point of view of the audience. *Wilder D. Bancroft*

The Textile Fibers. *By J. Merritt Matthews. Third edition. 23 × 15 cm; pp. iii + 630. New York: John Wiley & Sons, 1913. Price, $4.00 net.*—The subject is treated under the headings: classification of the textile fibers; wool and hair fibers; the chemical nature and properties of wool and hair fibers; shoddy and wool substitutes; minor hair fibers; origin and cultivation of silk; physical properties of silk; chemical nature and properties of silk; the vegetable fibers; cotton; the physical structure and properties of cotton; chemical properties of cotton cellulose; mercerized cotton; the minor seed-hairs; artificial silks; linen; jute, ramie, hemp, and minor vegetable fibers; analysis of the textile fibers; analysis of textile fabrics and yarns; bibliography of the textile fibers.

In the preface the author says: "Unfortunately, the subject of the textile fibres has been lamentably neglected by chemists, although there is abundant indication that a fertile field of research is open to chemists in this direction, and such work would have not only a scientific value, but would also be of great industrial worth. There is, as yet, relatively little known concerning the chemical constituents of the fibres, and the manner in which the varying chemical conditions of bleaching and dyeing and other chemical treatments affect the composition and properties of these constituents. The action of various chemical agents on the fibre as an individual has been very imperfectly studied. More work has been done in the microscopical field concerning the properties of the fibres, but even here the knowledge is very incomplete and disjointed, and especial attention is drawn to the fact that there is yet a large amount of work to be done in the microchemistry of the subject.

"The author has endeavored to emphasize throughout this volume the importance of the study of the fibre as an individual, for in many cases it is misleading to assume that the behavior of the individual fibre is identical with that of a large mass of fibres in the form of yarn or cloth. In the latter case, the difference in physical condition and the action of mechanical forces have an important influence. By going back to the study of the individual fibre as a basis, many explanations can be given which could not otherwise be discovered."

The author covers quite a range of topics. On p. 69 he points out that if fabrics of chlorinated and untreated wool be rubbed together, a considerable electric charge will be formed. This property of chlorinated wool formed the basis of a patented "electric" belt. With this possibility before one it is rather distressing to learn, from the next sentence, that garments of chlorinated wool do not wear well and are deteriorated rapidly by laundering. On p. 126 we read that "another property of silk, and one which is peculiar to this fibre, is what is termed its scroop; this refers to the crackling sound emitted when the fibre is squeezed or pressed. To this property is due the well-known rustle of silken fabrics. The scroop of silk does not appear to be an inherent property of the fibre itself, but is acquired when the silk is worked in a bath of dilute acid (acetic or tartaric) and dried without washing. A satisfactory explanation to account for the scroop has not yet been given; it is probably due to the acid hardening the surface of the fibre. Mercerized cotton can also be given a somewhat similar scroop by such a treatment with dilute acetic acid. Wool, under certain conditions of treatment, can also be given this silk-like scroop in some degree, as, for instance, when it is treated with chloride of lime solution or with strong caustic alkalies."

Under mercerization, p. 328, we read that "Boucart gives the following reasons why only long-stapled cotton, and that only in particular counts, gives good results on mercerization: A simple thread consists of a sort of twisted wick composed of nearly parallel fibres. The twist depends, as regards the angles it makes with the length of the thread, both upon the kind of cotton and upon the count of the yarn. Of the two sorts of simple yarns, warp-yarns have more cohesion among their elements than tensile strength, while the reverse is the case with the weft-yarns. The result is that under gradually increasing tension weft-fibres slide past one another without breaking, but warp-fibres break before any such occurrence takes place. The degree of twist also depends on the mean staple, and the angle between the thread and the axis at any point is proportional to the length of the thread. The degree of twist which is required to make the cohesion exceed the tensile strength depends naturally on the strength of the fibre. Hence the greater the angle the thread makes with that axis, the less is the effect of the tension, and if any portion of the fibre is at right angles to the axis it is not affected by the tension at all. Hence a simple warp-thread can only receive a medium amount of gloss from mercerization, this is less as the twist is greater. Slightly twisted threads should give the best lustre, but if the cohesion of the fibres is less than the contractile force exerted by the mercerizing, the fibres slip past each other and no lustre is produced. But if the weft-threads are fixed, as in piece goods, they take a better lustre than the warp, although the latter is usually made of better cotton. Short-stapled cotton acquires a less degree of lustre because it must be more tightly twisted. The best lustre of all is obtained with two-fold twist, in which the outer fibres lie parallel to the axis, and the yarn should be well singed to remove projecting fibres.

"The quality of being mercerized is not an inherent property of any special variety of cotton, as was formerly supposed to be the case; any variety of cotton is capable of mercerization, the essential being that the fibre shall be maintained in a state of tension. In order that this condition be realized with short-stapled fibres, the yarn operated upon must be tightly twisted in order to present sufficient cohesion among the individual fibres to allow of the high tension required; this, on the other hand, prevents an even and thorough penetration of the caustic alkali into the substance of the fibre, so that, on the whole, the results obtained with short-stapled fibres are not at all comparable with those of the long-stapled varieties."

While the preceding paragraphs are clear and to the point, the following one, p. 275, seems to mean nothing at all: "Regarded from the point of view of the ionic theory, cellulose is considered as a molecular aggregate consisting of a mixture of ions of varying dimensions. Hence, cellulose as a typical colloid has no definite reactive unit as a body which takes the crystalline form, nor a fixed molecular constitution which may be represented in the limits of a constitutional formula; for the cellulose molecule cannot be regarded as a static unit, but rather as a dynamic equilibrium; its reacting unit at any time being a function of the conditions surrounding it. This view of the constitution of cellulose has been advanced by C. F. Cross."

It is a pleasure to pass from this bit of esoteric fluency to a more characteristic passage, p. 405. "The chief chemical difference between jute and the pure cellulose fibres is in the ability of the former to combine directly with basic dyestuffs. In fact it acts in this respect similar to cotton which has been mordanted with tannic acid. Jute is also more sensitive to the action of chemicals in general than cotton or linen. On this account it cannot be bleached with much success, as treatment with alkalies and bleaching powder weakens and disintegrates the fibre to a considerable extent. The jute fibre is relatively weak when compared with other bast fibres, and the chief reasons for its prominence among the textile fibres are its fineness, silk-like lustre, and adaptability for spinning. The plant is also easy to cultivate and returns a large yield of fibre. The chief defect of jute is its lack of durability; when exposed to dampness it rapidly deteriorates; and even under ordinary conditions of wear, the fibre gradually becomes brittle and loses much of its strength. The bleached fibre is especially liable to such deterioration; it gradually loses its whiteness, and, evidently due to oxidation, becomes stringy and yellowish brown in color." "It must be borne in mind that the jute fibre is a ligno-cellulose composed of cellulose units about 1/8 inch in length cemented together by lignone components. In bleaching processes where a full white is obtained, these lignone substances are removed and this leads to the structural disintegration of the fibre."

There is a paragraph on the adsorption theory of dyeing, p. 304; but the author belongs to the school which yearns for compounds in dyeing and in mercerization. Barring this shortcoming, the book is an interesting and valuable one.

Wilder D. Bancroft

The Electric Furnace. *By Alfred Stansfield. Second edition. 17 × 23 cm; pp. vii + 415. New York: McGraw-Hill Book Company, 1914. Price, $4.00 net.*—The first edition appeared in 1907 and contained 211 pages. The second edition has been so enlarged and rewritten as to be practically another book, though the admirable arrangement of the first edition is retained.

The chapter in the first edition on production of iron and steel in the electric furnace has expanded to three: one on production of pig iron, one on production of steel from metallic ingredients, and one on direct production of steel from iron ore. That on "other uses of the electric furnace" is now divided into five: ferro-alloys and silicon, graphite and carbides, electric smelting of zinc and other metals, electrolysis and electrolytic processes, and miscellaneous uses. A chapter on laboratory furnaces and one on operation of furnaces have been added.

The book aims at completeness, and comes pretty near the mark. Yet there are omissions. We might fairly expect to find mention of the Hoskins and the Helberger furnaces, and the treatment of laboratory furnaces might well have been more full. Snyder's designs for zinc furnaces get several pages, while his direct arc furnace in use for melting steel is not mentioned. In a good many other cases furnaces that never got beyond the paper stage get a good deal of attention, and it is hard to tell from the text whether a process or furnace is a commercial success or not. One would gather that Acker cells, Pauling nitrogen furnaces and furnaces for the production of siloxicon itself and not merely as a by-product of carborundum, are in operation at present.

It is worth while to include in such a book furnaces that did not survive, and even schemes that were never tried, for historical and theoretical completeness, or because of the promise of future development. Yet it ought to be made clear when a furnace is mentioned for one of these reasons.

Promise of future development is doubtless the reason for the space given to zinc furnaces and to production of steel direct from ore, but it would seem that electric furnaces for heat treatment of steel, for brass melting and for melting glass also deserve mention on that score.

The description of mechanical details of furnace construction is useful. Sometimes one might wish for more information on a furnace or a process, but in most cases this is not the author's fault. He would doubtless have been glad to give us a full description of the aluminum furnaces at Niagara, but that would require powers of divination.

Carborundum fire-sand is said (pp. 65, 297) to be amorphous silicon carbide, and not identical with siloxicon. This is quite certainly incorrect.

Thermochemical data from J. W. Richards and electrode data from Carl Hering are given in quantity.

The book is primarily a text-book for college students, and is written as a professor would naturally write. It is quite a contrast to the essentially commercial atmosphere of the other recent electric-furnace book—von Baur's translation of Rodenhauser and Schoenawa's "Electric Furnaces in the Iron and Steel Industry." Yet those commercially interested in electric furnaces will find much in it worth their while.

The first edition was far and away the best book in its line when published. Much more has been written on the electric furnace since then, so that the second edition does not stand out as preëminently as did the first, but is still a worthy successor to it. *H. W. Gillett*

The Application of Physico-chemical Theory to Technical Processes and Manufacturing Methods. *By R. Kremann. Translated by Harold E. Potts. 15 × 22 cm; pp. xv + 212. New York: D. Van Nostrand Co., 1913. Price, $3.00.*—In the preface the author says: "Physical Chemistry used to be considered a somewhat theoretical branch of study, but it has recently developed in such a way as to explain many of the empirical observations of technology and to prove extremely suggestive of many new methods. Such a tendency may be considered one of the highest aims of scientific research. The young chemist frequently feels that in his first few terms and I have found that of all the problems of physical chemistry the beginner shows most interest in those which have some bearing on technical questions."

The subject is treated under the headings: the two fundamental laws of the mechanical theory of heat; reaction velocity and catalytes; other special applications of the law of mass action—the influence of temperature on the equilibrium constant; dissociation pressure—the phase rule; the application of the phase rule to solid-liquid systems; transformation phenomena in hydraulic binding agents; other applications of the phase rule—the distribution law—adsorption compounds—reciprocal pairs of salts.

Among the special topics taken up are: the Deacon process; the contact process for sulphuric acid; the chamber process for sulphuric acid; the manufacture of nitric acid, of ether, and of soap; the caustification of sodium carbonate; lime burning; Nordhaüsen sulphuric acid; roasting lead; the reactions in the blast furnace; the Pattinson process; the formation of iron and steel; the production of nickel matte; the drying of linseed oil; the conversion of oleic acid into stearic acid; vitrification and devitrification; plaster of Paris; the setting and hardening of Portland cement; the weathering of clay; the theory of dyeing; the vulcanization of rubber; the Parkes process; the ammonia-soda process; the formation of saltpetre from Chili saltpetre and potash; the ideal efficiency of the steam engine; the gas engine; producer gas; water gas.

The author has covered a great deal of ground and has covered it well in most cases. There is some confusion on p. 30 in regard to reduction with carbon, and the author has treated iron and carbon, p. 145, on the erroneous assumption that cementite is never a stable phase; but these are excusable errors. As a typical case of good work, I quote from the admirable discussion, p. 74, of devitrification.

"Let us now consider the relation between spontaneous crystallization power, the velocity of crystallization, and the viscosity. The viscosity of the liquid increases with the supercooling and frequently in a small range of temperature passes through all values from those of a syrupy liquid to those of a solid mass which is not deformed by the action of small forces. When the temperature is further lowered the mass becomes hard and brittle; this solidification occurs about 90° below the melting point.... After rapidly cooling past the temperature range in which numerous crystallization centres are formed, the viscosity is very high. No crystallization centres are then formed in the brittle vitreous mass. If these have formed during the supercooling they will still not grow in this temperature range, owing to the extraordinarily slow velocity of crystallization. Thus within this temperature range the substance is highly stable. If the viscosity is very high even at the melting point, as is the case in many silicates rich in alumina, the maximum values of the spontaneous crystallization power and the crystallization velocity are small. The shape of the viscosity curve and its relative position to the spontaneous crystallization power curve determines whether a substance can be drawn out into thin threads or blown into vessels in the same way as glass. For a substance to be worked like glass it is a necessary condition that the number of crystallization centres must be very small in the temperature range in which the viscosity possesses the value best suited for working the viscous liquid. It is also important that the viscosity curve should not rise too steeply since otherwise the temperature range, in which the liquid has the most suitable viscosity, is too small, which naturally renders working very difficult. For many purposes it is important to be able to control the number of crystallization centres forming in a supercooled melt. If this can be done we can obtain any substance as a crystal conglomerate or in the amorphous state, as may be desired. Explosive antimony is the only one of the metals which has been obtained in this state. A magnetic or electric field or radium radiation has no influence here, but a great effect is produced by substances dissolved in the melt. Some of these added substances depress the number of crystallization centres to zero even in the temperature range of the maximum.

Others highly increase the number without changing the temperature of the maximum. Finally some exert practically no action in small quantities. Indifferent, *i. e.*, insoluble, substances may exert no action or an increasing or diminishing action; platinum nearly always increases the action."

Wilder D. Bancroft

Quantitative Analysis by Electrolysis. *By Alexander Classen. Translated from the fifth German edition by William T. Hall. 23 × 16 cm; pp. v + 308. New York: John Wiley & Sons, 1913. Price: $2.50 net.*—In the preface the author says: "Successive editions contained the innovations and improvements that were made in the years 1882 to 1897 until, in the fourth edition, a section was introduced which contained theoretical considerations based upon the then new theory of solutions. During the last decade, however, the development of electrochemical methods not only on the practical side but also as a result of the development of physical chemistry, especially electrochemistry, has placed electro-analysis upon a scientific foundation. The advances in both practical and theoretical directions have been so marked that it has been necessary to revise the book thoroughly, and the present edition may be regarded as practically a new book."

There are a great many statements in the introductory chapter which might better have been worded differently. The author says, p. 5, that when a sodium chloride solution is electrolyzed, "sodium ions are changed into the element sodium, which in accordance with its chemical nature, decomposes water and sets free hydrogen." That conception was overthrown by LeBlanc twenty years ago. On p. 21 is a statement that "as both electromotive force and potential are measured in volts, and both have the same numerical value, the three terms potential, electromotive force and voltage are used synonymously." That is a painfully sloppy way of doing things and the translator might at least have used the right terms. We should then have been spared the statement, p. 31, that "the resistance of the voltmeter is so great that nearly all of the current continues to pass through the cell with a practically unchanged electromotive force." In spite of the fact that 92 pages are devoted to the theoretical introduction, it is evident, p. 191, that the author is not clear at all as to the theory of the electrolytic separation of two metals. He has mastered the theory of constant voltage separations, but the theory of constant current separations is overlooked entirely. Perhaps it is on this account that the author says, p. 57, that "much remains to be explained in the theory of rapid electrolysis." On p. 131 there is no justification for the statement that the "deposition of antimony upon the cathode is really the result of a secondary reaction, which is the action of the discharged sodium ions upon the sodium thioantimoniate." It is true that the author qualifies this statement by the words "according to Ost and Klapproth;" but, practically, Classen adopts it.

The subject matter of the book is good, of course, and the book is a valuable one. The presentation is not so good because of Classen's too obvious desire to make people believe that most of the important improvements have originated with him. As a typical instance, take what is said, p. 97, about the introduction of rapid electrolytic methods. In a sense it is all true; but it conveys an absolutely false impression of the facts. On p. 57 it is stated that "after the experiments performed in the author's laboratory and elsewhere had removed all doubt concerning the value of the new method of working, the authorities at Aachen consented to provide means for fitting up the first large laboratory with the necessary apparatus for carrying out rapid electrolysis." A statement of this sort is quite inexcusable because the author must have heard of the Pennsylvania laboratory. When a man has done as much good work as Classen has done, it is a pity that he should reach out for laurels which do not belong to him.

Wilder D. Bancroft

Lehrbuch der Thermodynamik. *By J. D. van der Waals and P. Kohnstamm. Vol. II. 17 × 23 cm; pp. 645. Leipzig: Johann Ambrosius Barth., 1912. Price: 24 marks.*—The volume deals with heterogeneous equilibria for the most part and consequently the first chapter is devoted to the phase rule. It is delightful to note the calm way in which van der Waals straightens out the squabbles about the phase rule which have come up so unnecessarily in recent years. The most striking characteristic of the book is its calm sanity. On p. 97 the authors say that "one is in no wise justified in assuming that the state of a dissolved substance is at all like an ideal gas.... It is clear that when we compress a solution, the pressure which resists the compresssion is not due merely to the molecules of the solute but also to those of the solvent; in fact, chiefly to them because they are present in much greater numbers. One is also not justified in attributing the osmotic pressure to the molecules of the solute. In the case of equilibrium with a membrane the pressure upon the membrane and on the walls of the cell is due chiefly to the molecules of the solvent. This point of view eliminates the much-discussed question why a thin beaker does not burst when containing a solution which may exert an osmotic pressure of many atmospheres. The solution actually exerts a pressure of one atmosphere on the glass wall. That its osmotic pressure is fifty atmospheres, for instance, merely means that one must exert this pressure on it to keep it in equilibrium with a semipermeable membrane, on the other side of which is pure solvent at atmospheric pressure."

When discussing the Soret phenomenon, p. 102, the authors point out that a stationary state is reached but not a state of equilibrium; consequently the thermodynamic potential is not necessarily the same in the two portions of the tube. The reviewer regrets that they did not go one step farther and at least indicate the criteria for the stationary state when one takes into account the practical imcompressibility of liquids.

In the last part of the book, the authors discuss systems in which the effect of external forces and of chemical forces are not ignored. They do not discuss capillarity but they take up the effect of gravity and of electromotive force; they also consider the case of electrolytic dissociation.

Wilder D. Bancroft

EXPERIMENTS ON WHITE LEAD

BY R. STUART OWENS

This work was undertaken to determine, if possible, in what way and to what extent the character of precipitated white lead varied with the conditions of precipitation. The Dutch process for making white lead seems still to be the standard one although it is slow and consequently ties up a large amount of capital. Holley[1] cites the Carter process, the Rowley process, and the Matheson process as rapid processes which are on a commercial basis. No electrolytic process seems to be a commercial success as yet, though the rapidity and control of corrosion is a strong argument in favor of an electrolytic process. The difficulty is that the electrolytic white lead is probably coarser in grain and consequently lacks covering power. It also requires a large amount of oil. This latter difficulty is said to be overcome by a process patented in 1907, by Mr. E. A. Sperry, the substance of which is as follows:

"For the electrolytic production of a lead pigment a previous electrolytic treatment of the lead is stated to be highly advantageous, whereby the lead is used as anode and deposited on the cathode, the cathode product being then used for making the pigment. For example, white lead produced electrolytically absorbs as high as 20 drops of oil per gram to bring it to a standard paste, whereas, by using the cathode product of the first electrolysis as anode in the second, the particles may be rendered harder, thus forming crystals which work smoother under the brush, as well as possessing other qualities which make it more desirable. Probably the most distinguishing feature is that the white lead so formed is said to bring down the oil absorption to between 3 or 4 drops per gram, a reduction of something over 75 percent in the amount of oil required."

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[1] "The Lead and Zinc Pigments," 74, 85, 101 (1909).

It is difficult to see how the precipitation of an electrolytically formed lead salt can depend on the physical characteristics of the lead anode, though the efficiency of corrosion might be affected. Unless the first electrolysis caused a refining of the lead, it is extremely improbable that the results are due to the alleged cause.

White lead is known to be a definite compound,[1]

$$(PbCO_3)_2PbO_2H_2,$$

and the commercial white leads do not vary much from this composition. Experiments were therefore made on the precipitation of lead carbonate, lead hydroxide, and basic lead carbonate, from solutions of varying concentrations and at varying temperatures. Solutions of sodium hydroxide, sodium carbonate, and lead acetate were made up of concentrations varying from normal to sixty-fourth normal—the word normal being used in the sense of equivalent concentration and not of molecular concentration. For this work a normal solution of sodium carbonate or caustic soda contains twenty-three grams of sodium to the liter and a normal solution of lead acetate contains 103.5 grams of lead to the liter. Strictly speaking, only the normal solutions were made up accurately, the others being prepared by adding 500 cc. water to 500 cc of the preceding solution. The error due to contraction or expansion is presumably negligible for work of this type and has been so considered.

It seemed desirable to find out what variations in crystal size might be expected. Since moderately high concentrations of the precipitating agents and moderately low temperatures are favorable in general to the production of small crystals, precipitations were first made from normal solutions at room temperature and from *N*/16 solutions at higher temperatures. The precipitated crystals were examined in the mother liquor under the microscope, using an eyepiece with a micrometer scale. The data are given in Table I:

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[1] Hawley: Jour. Phys. Chem., 10, 654 (1906).

TABLE I

Precipitate	Solution	Temperature	Diameter mm
Lead carbonate	*N*/1	20°	0.0010
Lead carbonate	*N*/16	80°	0.0023
Lead hydroxide	*N*/1	20°	0.0010
Lead hydroxide	*N*/16	80°	0.0375

The lead carbonate precipitates vary in a ratio of about one to two and the lead hydroxide precipitates in a ration of nearly one to forty. A series of runs was therefore made. The solutions were all precipitated by pouring 50 cc lead acetate solution into a beaker in a constant temperature water bath and adding an equal volume of the corresponding hydroxide or carbonate solution to it. The temperature given is that of the water bath and not necessarily of the solutions. During precipitation the solutions were stirred by an electrically driven stirrer. The importance of this has been emphasized by Free.[1] The data for lead carbonate are given in Table II:

TABLE II

Lead Carbonate

Solution	Temperature	Diameter in mm/1000
N/1	20°	1.0, 1.2, 1.0
N/2	20°	1.4, 1.4
N/4	20°	1.8, 1.8
N/8	20°	2.0
N/8	60°	2.0
N/16	20°	2.0
N/16	74°	2.0
N/16	80°	2.3
N/32	20°	2.3
N/32	45°	2.4
N/32	70°	2.5
N/64	70°	Milky solution

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[1] Jour. Phys. Chem., 13, 128 (1909).

The particles from the $N/2$ solutions settled more rapidly than those from the $N/1$ solutions. The particles from the $N/4$ solutions settled rapidly and appeared as rounded masses. From the $N/8$ solutions rounded egg-shaped masses were obtained. With $N/16$ solutions a very uniform field of round-shaped particles was obtained at 20° while at 70° and 80° the particles were slightly transparent. With $N/32$ solutions at 20° and 45° a milky liquid was obtained, which required over twenty-four hours to clear, rounded globular shaped particles settling. When precipitated at 70° the solution cleared in about twelve hours, rounded globular shaped particles separating. With $N/64$ solutions no precipitates were obtained from the slightly milky solutions when allowed to stand for three days at room temperature, regardless of the temperature of precipitation.

These results are in harmony with those obtained by Free[1] in his work on lead chromate. Free found that "in the very dilute solutions lead chromate remains in colloidal solution for several days," and that the largest crystals are obtained in hot and dilute solutions. The mean size of the particles is of course given by the amount of lead carbonate, in excess of that required to saturate, divided by the number of particles. If the number of particles decreased proportionally to the supersaturation, the size of the particles would remain constant. If the number of particles falls off more rapidly than the supersaturation, the size of the particles will increase with increasing dilution of the reacting solutions; the size of the particles will decrease if the number falls off less rapidly than the supersaturation. In concentrated solutions the precipitation takes place so rapidly that the crystals do not have time to grow, which is another way of saying that the number of nuclei is relatively high. With more dilute solutions we usually say that the crystals have time to grow; but we could equally well say that there are relatively fewer nuclei formed. With very dilute solutions the crystals are

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[1] Jour. Phys. Chem., 13, 130 (1909).

not large because there is nothing left in the solution after the nuclei are formed. In other words, the number of the nuclei does not decrease anything like so rapidly as the supersaturation. This is not inconsistent with the fact that the mineralogists obtain crystals of insoluble substances by allowing dilute solutions to diffuse together slowly. A colloidal solution may perfectly well give rise to relatively large crystals in the course of sufficient time, because the very fine particles are more soluble than the relatively large crystals. On the other hand, it is not yet clear how one could predict that the relative number of particles will first decrease and then increase with decreasing supersaturation. It is not at all what one would expect from Tammann's experiments on the behavior of supercooled liquids.

The data for lead hydroxide are given in Table III:

TABLE III

Lead Hydroxide

Solution	Temperature	Diameter in mm/1000
$N/1$	20°	1.0, 1.0
$N/2$	20°	1.5, 1.5
$N/4$	20°	7.5 (1.5 wide)
$N/4$	48°	12.5
$N/4$	70°	15.0
$N/8$	20°	25.0
$N/8$	66°	17.5 (crosses)
$N/8$	66°	12.5 (cubes)
$N/8$	47°	50–7.5
$N/8$	33°	30 (white)
$N/8$	28°	30 (white)
$N/16$	20°	37.5 (needles)
$N/16$	60°	37.5 (no needles)
$N/32$	20°	Whitish precipitate

With $N/2$ solutions rounded masses of lead hydroxide were obtained. With $N/4$ solutions a mixture of needles and skeletons were obtained at 20°; at 48° a uniform field of crosses was obtained; and at 70° a less uniform field composed chiefly of crosses with pointed ends. With $N/8$ solutions there were only crosses at 20° but they were filled out better than with the more concentrated solutions. At 66° there was a slightly yellow precipitate and the crosses were nearly filled out, so that there was a gradual gradation from crosses to lop-sided cubes. At 47° the yellowish precipitate was lighter than at 66°. The crystals were crosses of varying sizes; but only a few were nearly filled out. At 33° there were hardly any well-formed crystals, mostly all being skeletons. At 28° there were no cubes. Both at 28° and 33° there was no yellow precipitate. With $N/16$ solutions at 20° the crystals were all long yellowish needles of different sizes. At 60° there was a distinct yellow color but no crystal needles. With $N/32$ solutions at 20° a whitish precipitate was obtained but no distinct crystals were noted.

The general conclusions from the experiments given in Tables II and III are as follows:

1. The size of the precipitate varies with the conditions under which it is formed.
2. As with other substances, larger particles of lead carbonate and of lead hydroxide are obtained from hot, dilute solutions than from cold, concentrated ones.
3. The lead carbonate could not be obtained as definite crystals, the prevailing form being rather that of an egg. The globules of the lead carbonate, thus produced, appeared translucent under the microscope.
4. The lead hydroxide was obtained in definite crystalline form, varying from needles to what appeared to be lop-sided cubes. The size of the particles could be varied much more than in the case of the lead carbonate.

Some years ago it was pointed out[1] that one could start with a coarse and a fine lead hydroxide and a coarse and a fine lead carbonate and could combine these in four different ways, thereby getting the possibility of four different white leads. This experiment was tried, starting with lead hydrox-

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[1] Bancroft: Trans. Am. Electrochem. Soc., 14, 150 (1908).

ide and lead carbonate precipitated at 20° from *N*/1, *N*/8 and *N*/16 solutions. The moist precipitates were mixed in the proper proportions, covered with dilute sodium acetate solution, stirred occasionally, and left at room temperature until equilibrium was reached. Tests were made from time to time to see whether any particles of the original substances remained. Equilibrium was always reached inside of twenty-four hours. All possible combinations were tested.

The resulting particles of white lead did not seem to possess a definite crystalline form and were all of the same size, shape, etc., irrespective of the size of the original reacting particles. The average size of the particles was 0.0015 mm; while most of them were rounded, a good many were elliptical and all appeared translucent. The most probable explanation for this result is that the solid lead carbonate and lead hydroxide did not react directly to any appreciable extent and that the white lead was formed by the interaction of lead carbonate and lead hydroxide dissolved in the dilute sodium acetate solution. Experiments were also made with 5*N*, *N*/1, *N*/5, and *N*/50 sodium acetate solutions at 20°; with practically the same results. At higher temperatures equilibrium was reached more rapidly; while there seemed to be a slight difference in the size of the particles, the amount of change could not be estimated. This is probably due to the fact that the higher temperature and the more rapid reaction counterbalance each other.

It was next decided to mix the sodium hydroxide and the sodium carbonate solutions in the ratio of one to two, and then to pour this mixed solution into an equivalent lead acetate solution, varying the concentrations and the temperature. The data are given in Table IV.

Experiments were made only at the two extreme temperatures because it was thought that sufficient data would be obtained thereby for present purposes. It is not clear why the particles should be smaller at the higher temperature than at the lower. It is possible that the agglomeration at the higher temperature has given rise to a denser form.

The time at my disposal did not permit of a further study of this unexpected phenomenon. The data show that the average size of the particles of white lead can be varied from 0.0008 mm to 0.0020 mm without having recourse to solutions more dilute than $N/16$. While this change in size is not very large, it shows the possibility of making a number of white leads, having different physical properties, though identical in chemical composition.

TABLE IV

White Lead

Lead acetate solution	Diameter in mm/1000		Appearance
	20°	98°	
$N/1$	1.25	0.8	Rounded and translucent
$N/2$	1.5	1.0	Rounded and translucent
$N/4$	2.0	1.5	Rounded and translucent
$N/8$	2.0	1.6	Rounded and translucent
$N/16$	1.8	1.6	Rounded and translucent
$N/32$	0.2	1.6	Rounded and translucent
$N/64$	0.2	0.2	Rounded and translucent

The next step was to determine which size of particle was best for commercial purposes; but owing to lack of time, this point was not worked out thoroughly. Covering power, durability, oil absorption, and the ease with which the pigment may be worked under the brush should be considered. The oil absorption was first tested on the laboratory scale; working under the brush was then tested, and a few pieces of wood were painted so as to obtain some idea of the covering power, but nothing whatever was done in the way of testing durability.

Correspondence as to the best method of determining oil absorption brought out very little except advice to consult a practical painter. Anybody who has had any experience with a so-called practical painter knows that it would have been an absolute waste of time to follow this advice. Consequently, a method of determining oil absorption was worked out which had the merit of giving very interesting results and which probably possessed a fair relative accuracy. Of course no method can be called accurate which depends in such a way on the sense of touch. The method employed was to use a convenient receptacle into which any known weight of the dried white lead was placed. The linseed oil was allowed to run in from a burette until a certain consistency was reached. In this work a three-inch agate mortar and pestle was used. Five or ten grams of white lead were placed in the mortar and the oil was allowed to drop into the pigment with which it was carefully mixed. The process was continued through the granular state until the mixture finally became pasty and sticky. When the mass became so sticky that the mortar could be lifted by the pestle adhering to the paint, the cubic centimeters of added oil were noted, as this seemed to be a fairly accurate reproducible end-point. This end-point differs very much from that selected by the painter; but each end-point could be expressed in terms of the other by anybody who knew what the painter's end-point was.

The data are given in Table V:

TABLE V

Oil absorption with precipitated white lead

Size of crystals in mm/1000	cc oil used	Pigment in grams
2.2	1.1	5
2.0	1.0	5
1.6	0.9	5
1.4	0.85	5
0.8	0.55	5

These results show that the amount of oil needed does not increase proportionately to the size of the particles; but it also shows conclusively that there is a marked difference in the amount of oil needed to produce the given end-point.

The following qualitative observations were made on the covering power as affected by size of particles. Paints made from the larger particles and from the smaller ones were applied to pieces of wood previously painted with a black of unknown composition. A given weight of dry white lead was mixed with a given number of cubic centimeters of oil and all of the same was applied with a clean brush to a board of standard size. After drying for twenty-four hours, the pieces of wood were examined and it was found that the paint made from the smaller particles was far superior to that made from the larger ones. A second coat of paint was given to the piece of wood which had been painted with paint made of the larger particles; but after drying the coating was thought still to be inferior to that on the other sample. It was therefore decided that one coat of paint made from the smaller particles was certainly superior to two coats of the paint made from the larger particles. The reason for this difference is perhaps to be found in the fact that the pigment precipitated from the lead acetate solution consisted of translucent rounded particles which seemed to possess no definite crystalline form. In a particle like this, the covering power is due chiefly to the rim of the globule and consequently the covering power will be less the greater the relative proportion of translucent center. Bedson[1] says that "white lead is a white, earthy, heavy powder, which, from its behavior to polarized light, undoubtedly possesses a crystalline structure. Examined under the microscope, it appears to consist of rounded, circular, or oval grains. The grains are transparent; they vary in diameter from 0.0025 to 0.0009 mm."

As for the property of working under the brush, it can only be stated that the smaller particles seemed to work better. A definite statement could be made only after experiments by an expert with much larger amounts of pigment.

Since the small particles make the best pigment so far as these tests are concerned, it seemed desirable to make a few observations on commercial white leads. On examina-

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[1] "Thorpe's Dictionary of Applied Chemistry," 2nd Ed., 3, 287 (1912).

tion of some pigments made by processes similar to the Dutch process, it was found that the product varied considerably in the size of the particles contained; but that the average run was probably about 0.0014 mm. It should be noticed that it is not necessarily desirable to have the particles of uniform size. Approximately circular particles will pack more closely and consequently will have greater covering power when of two or more sizes than when uniform.

Products obtained from outside sources may be given as follows:

Eagle White Lead Company: Average size 0.0022 mm; composed of rounded and fragmental pieces.

Acme White Lead Company: Even product averaging about 0.0024 mm.

Matheson White Lead Company: Average size 0.0022 mm; mostly well-rounded masses.

Carter White Lead Company: Average size 0.0018 to 0.0020 mm; rounded particles uniformly smaller than other varieties examined.

National White Lead Company: Average size 0.0020 mm; a very scaly product of irregular shapes.

It was very interesting to note that when equal volumes were placed in the sample bottles, the bottles containing the smaller and the larger particles could be differentiated by weight alone.

The last experiment was to make some white lead electrolytically on the laboratory scale. The Woltereck and Luckow methods were taken as fairly typical. Data for the experiments were obtained as far as possible from the United States patents:

1. *Woltereck Patent*, No. 589,801:

Electrolyte contains 10–15 percent of a mixture of 80 parts CH_3CO_2Na and 20 parts $NaHCO_3$.

Carbon dioxide introduced at bottom of vessel; solution stirred.

Lead electrodes; current density of one ampere per square decimeter.

Results: Much oxide of lead thrown down with the white lead; anode badly pitted.

Size of crystals = 0.002 mm.

2. *Luckow Patent,* No. 627,662.

Electrolyte contains 0.3–3.0 percent of a mixture of 80 parts $NaClO_3$ and 20 parts Na_2CO_3.

Sodium carbonate added from time to time; solution stirred.

Lead electrodes; current density of one-half ampere per square decimeter.

Results: Anodes in fairly good condition.

Size of crystals = 0.0022 mm.

From these two tests it will be seen that the sizes of the particles are what one would expect from slow precipitation. The fact that the particles are much the same size as those obtained by the rapid processes does not prove that the electrolytic white lead is as good as the other because no tests were made on the density, the oil absorption, etc. These experiments do prove that these two electrolytic methods are not run under conditions which give the best precipitate of white lead.

The general results of this paper are:

1. Lead hydroxide can be precipitated with a definite crystalline form and the size of the crystals can be varied between rather wide limits.

2. Lead carbonate was not precipitated in any definite crystalline form. It is probable that the particles consist of aggregates of very small crystals. The size of the particles can be varied between narrow limits.

3. When a mixture of particles of lead carbonate and lead hydroxide are allowed to stand together under a sodium acetate solution, the particles of white lead have the same size, no matter what the size of the particles of the reacting salts.

4. When a suitable mixture of sodium hydroxide and sodium carbonate is added to a solution of lead acetate, white lead is precipitated and the size of the particles can be varied between rather narrow limits.

5. White lead thus prepared does not show any definite crystalline form; it seems to consist of rounded translucent particles.

6. Rapid precipitation gives smaller particles and slow precipitation gives larger particles.

7. The commercial samples and those produced in the laboratory by electrolytic means had particles corresponding in size to those obtained by slow precipitation.

8. The oil absorption, as tested, is much less with small particles of white lead than with the larger particles.

9. The paint made from a pigment consisting of smaller particles was superior to that produced from a pigment consisting of larger particles.

10. Uniformity in size of particles is not necessarily an advantage in a paint.

The experimental work was done in the spring of 1909; but publication has been delayed. The work was suggested by Professor Bancroft and was carried out under his supervision.

Cornell University

THE QUANTITY OF RESIDUAL VALENCE POSSESSED BY VARIOUS MOLECULES

BY A. P. MATHEWS

All, or nearly all, molecules possess some power of combining with molecules of the same or different kinds. This combining power is called the residual valence, or affinity, of the molecule. Thus ammonia, NH_3, will unite with water or acids, a molecule of hemoglobin with oxygen, glucose and probably all salts with water when they dissolve in it, and other examples of this power of molecular union might be given.

The importance of residual valence to the molecule is generally recognized. It is probable that, with the possible exception of ionic reactions, these molecular unions precede, and are a necessary condition for, most chemical interactions between molecules; for molecules do not seem to affect each other by simple contact, but only when they are united into a new molecule by chemical bonds. It would seem that it is only when they are thus united that the atoms of two molecules are able to interchange and undergo those rearrangements resulting in the birth of new molecular species.

The importance of residual valence makes it desirable to know how much of it is possessed by each species of molecule. Since it is possible that this amount may not always be the same even for the same species of molecule, a method must be used in determining the average amount which will examine the molecular system without disturbing it. For example not all the molecules of carbon dioxide may be in a condition to unite with water at the same instant. Many facts indicate that of all the molecules of oxygen in the air only a few, at any instant of time, are in a condition to unite with oxidizable substances. The number possessing residual valence is small. This changing molecular condition seems analogous to, and is very possibly essentially identical with, the varying condition of atoms of radium which only occasionally become radioactive and decompose. It is not impossible, on the electronic theory of valence, to ascribe the acquiring of additional or residual valence by the atoms of molecules to internal rearrangements of the electrons within the atoms, similar to that rearrangement which, in radioactive substances, leads to an explosion of the atom.

The method I have used to determine the quantity of residual valence is a physical one, based on the cohesion of molecules. While the method is not very accurate at present, owing to several doubtful points in the calculations, it probably places the molecules in the order in which they occur when arranged according to the amount of average residual valence they possess; and it will become more precise as the critical data are more accurately known and the cohesion or internal pressure more accurately determined. The method is as follows: The internal or cohesive pressure of a fluid is represented by the value a/V^2 of van der Waals' equation. In this expression V^2 represents how the cohesional attraction varies with the distance; and "a" is the "mass" factor of the attraction. Now "a" includes the factor N^2, N being the number of molecules in the volume V, and if "a" is divided by N^2 then the quotient represents the "mass" factor of the cohesional attraction of two molecules and it may be written M^2K to correspond with the mass factor of the gravitational attraction, m^2k, in which "m" is the gravitational mass and "k" the gravitational constant. The relationship was found[1] that M^2K is proportional to the two-thirds power of the product of the molecular weight by the number of valences in the molecule, or $M^2K = C(\text{Wt.} \times \text{Val.})^{2/3}$. How accurately this relationship holds is shown in Table I in which the value of "a" which is of course proportional to M^2K, and is the mean value computed from various formulas, is compared with the value of "a" computed from the molecular weight and the number of valences. The method of computing "a" was given in another paper.[2]

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[1] Mathews: Jour. Phys. Chem., 17, 181 (1913).

[2] Mathews: Ibid., 17, 603 (1913).

TABLE I

Comparison of "a" computed from the critical data, etc., with "a" computed from the molecular weight and valence. The figures represent dynes for gram mol amounts, multiplied by 10^{-12}

Substance	Mean value of "a"	$a = C(\text{Wt.} \times \text{Val.})^{2/3}$ ($C = 1.259 \times 10^{11}$)	Difference Actual	Difference Percent
H_2	0.311	0.317	—0.006	—1.89
N_2	1.836	1.842 (Val. = 2)	—0.006	—0.31
O_2	1.984	2.014 (Val. = 2)	—0.030	—1.5
n-Pentane	22.07	21.96	+0.11	+0.5
i-Pentane	21.41	21.96	—0.55	—2.2
n-Hexane	28.10	27.71	+0.39	+1.38
Heptane	34.82	33.80	+1.02	+3.06
Octane	41.94	40.17	+1.77	+4.4
Diisobutyl	40.01	40.17	—0.16	—0.4
Ether	19.94	20.46	—0.72	—0.32
Benzene	21.95	22.19	—0.24	—0.11
Chlor-benzene	23.26	22.94	+0.32	+0.14
Toluene	28.12	27.97	+0.15	+0.50
Metaxylene	34.08	34.06	—0.02	+0.06
Methyl formate	12.04	12.25	—0.21	—1.7
Methyl acetate	17.12	17.42	—0.30	—1.1
Methyl propionate	22.49	22.96	—0.47	—2.0
Ethyl acetate	22.84	22.96	—0.12	—0.5
Propyl formate	23.13	22.96	+0.17	+0.72
Methyl butyrate	29.53	28.84	+0.69	+2.4
Methyl iso-butyrate	28.27	28.84	—0.60	—2.1
Propyl acetate	28.95	28.84	+0.08	+0.3
Ethyl propionate	28.92	28.84	+0.05	+0.2
$SnCl_4$	32.58	32.58 (Val. = 16)	±0.00	±0.00

From the equation $a = C(\text{Wt.} \times \text{Val.})^{2/3}$, if M^2K, or "a," can be determined, and if C and the molecular weight are known, the total number of valences in the molecule can be calculated. If from this total number of valences there be subtracted the number which is known to exist in the molecule on the basis that hydrogen is univalent, oxygen bivalent, carbon quadrivalent and so on, the remainder may be supposed to constitute the *average* amount, or number, of extra or residual valences which the molecule possesses. It is this number which has been determined in this paper.

Granting that this number really represents the residual valence, the accuracy with which it can be determined will depend on the accuracy with which M^2K, C, the molecular weight and the number of valences reaching between the atoms can be determined. The molecular weight may be assumed to be normal for non-associating substances at the critical temperature; and we have to assume that the number of valences between the atoms are those which chemists usually assign to these elements. The determination of the constant C, however, is more difficult. It could be determined empirically if M^2K was known accurately for any substance of which the valence is fixed and certain. Hydrogen is the only element with an unchanging valence, but unfortunately the critical pressure of hydrogen is uncertain. Moreover, it cannot be assumed that the valence of hydrogen is exactly unity. There are several indications that a molecule of hydrogen has some residual valence although it is certainly small in amount. One such indication is the solubility of hydrogen in water. At the same pressure and temperature more molecules of hydrogen dissolve in water than of helium, and hydrogen is half as soluble as nitrogen which almost certainly has residual valence. If solubility involves residual valence, as it may, this means that hydrogen would have some residual valence. Its solubility in platinum may be interpreted in the same sense. The catalytic reducing action of platinum, nickel or other metals or metallic oxides in a hydrogen atmosphere is interpreted by Sabatier[1] to mean that a chemical union of the reacting substances occurs. Armstrong,[2] too, has expressed the opinion that hydrogen has a small amount of residual valence. For these reasons we cannot accurately determine C from hydrogen. Nevertheless I have calculated M^2K and C for hydrogen to show what the value of C would be if hydrogen were univalent.

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[1] Sabatier: Nobel Prize Address, p. 9, *et seq.;* Les Prix Nobel en 1912; La Méthode d'Hydrogénation directe par Catalyse.

[2] Armstrong: "Valency," Encyclopaedia Britannica, 11th Ed., 27, 848 (1911).

Using the critical data of T_c = 32.3 and P_c, 13 atmospheres as found by Olszewski; and d_c as 0.033 as determined by Dewar, the critical coefficient S, where $S = RT_c/P_cV_c$, is equal to 2.860. This value of S is, however, much lower than that of any other substance. Thus for O_2, S is 3.5; for N_2, 3.6; for N_2O, 3.4 and even for helium it is 3.13 according to Onnes. It is probable then that 2.86 is too low. The critical temperature and pressure have recently been determined by Buller[1] who finds $T_c = 31.95$; $P_c = 11$. With these values and $d_c = 0.033$ S computes 3.903, which is higher even than such complex substances as octane and is clearly too high. If S is calculated by my formula which gives a result within 1–2 percent in most cases, namely, $S^2 = R(d_1 - d_v)T_c^{1/2}/\text{-}(T_c - T)^{1/4}MP_c$, using Buller's values for P_c and T_c and taking d_1 as that of hydrogen at the melting point [—258.9° (Travers)] as 0.086 (Dewar) and disregarding the value of d_v at that temperature then S is computed as 3.517. If P_c were 11.5 atmospheres, and the uncertainty is at least half an atmosphere, S would be 3.365. I believe S of hydrogen may be taken as approximately that of oxygen or as 3.4. If S is assumed to be 3.4 then with P_c 11 and d_c 0.033, $a = (S^2 - S + 2)/(S - 2)\ P_cV_c^2 = 0.301 \times 10^{12}$. Dividing this by N^2 where $N = 6.062 \times 10^{23}$, M^2K for hydrogen would be 8.191×10^{-37} from which C is found to be 3.23×10^{-37}. If, however, S = 3.4 and P_c 13, then "a" would be 0.317×10^{12}, M^2K, 8.626×10^{-37} and C would be 3.45×10^{-37}. Since from Buller's results it is probable that P_c should be lower than 13 atmospheres, the value for M^2K is probably not far from correct so that C should be very nearly 3.23×10^{-37}.

Another simple substance from which a calculation of C might be made is methane, since the amount of its residual valence is certainly small and the total number of valences per molecule is very nearly 8. Unfortunately the critical density of methane is unknown and T_c and P_c have not been recently determined. However, if T_c is 191.2 and P_c is 54.9

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[1] Buller: Phys. Zeit., 14, 860–2 (1913).

(Olszewski) and if S be calculated by the formula already given using the value of the density of the liquid at —164° as 0.466 and disregarding the vapor density, S computes to be 3.318 which is probably not far wrong. From this "*a*" is found by the formula given above to be 3.025×10^{12}, M^2K is 8.232×10^{-38} and C is found to be 3.24×10^{-37} which is almost the same value as that computed from hydrogen.

The critical data of oxygen are known, but the calculation shows clearly that oxygen is monovalent in the elemental form, there being but two valences in the molecule. This unexpected conclusion makes it impossible to use oxygen for the determination of C until it can be shown from independent sources that oxygen in the elemental form is really monovalent. There is some residual valence also. But if the residual valence be disregarded and two valences only be postulated in the molecule, the value of C would be 3.43×10^{-37}.

The mean value of C determined from all the substances in Table VIII in my former paper was 3.45×10^{-37}, if Millikan's value of the number of molecules in a gram mol., namely 6.062×10^{23}, is used in the computation. Since in this calculation of C the molecules were not supposed to have residual valence, it is clear that an allowance for the presence of this valence would have the effect of lowering C, so that its true value must be somewhat less than 3.40×10^{-37}.

A way in which C can be independently determined was suggested by the relation between cohesion and gravitation.[1] In the formula $M^2K = C(\text{Wt.} \times \text{Val.})^{2/3}$ it is evident that M^2K is proportional to the $^2/_3$ds power of the gravitational mass of a molecule and when weight and valence are unity $M^2K = C$. It occurred to me that under these circumstances C might very possibly be nothing else than the factor $(m^2k)^{2/3}$ of a molecule of unity molecular weight. In this case "*m*" is the gravitational mass of such a molecule and "*k*" the gravitational constant. A computation of $(m^2k)^{2/3}$ using Millikan's recent determination of the number of mole-

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[1] Mathews: Jour. chim. phys., 1914.

cules in a gram mol, gave the result $(m^2k)^{1/4} = 3.20 \times 10^{-37}$ which is very close to the figures already obtained from methane and hydrogen, and somewhat less, as it ought to be, than the mean value of 3.45×10^{-37} which was obtained when residual valence was disregarded. In view of these facts I believe we may assume that 3.201×10^{-37} is the real value of C, although the theoretical basis of this relationship is still lacking, and proceed with the calculation of the total valence of a molecule on that assumption.

The value of M^2K is less satisfactory. It is here that the main uncertainty of the calculation lies. As I have already discussed the methods of calculating this value in my paper on the internal pressures of liquids I will not go into the question at this time further than to point out two or three considerations bearing on the probable accuracy of those figures. In all the formulas for "*a*" which have so far been proposed certain assumptions have been made. The one ordinarily made in van der Waals' method of computing "*a*" is that $b_c = V_c/3$. In the various methods I have proposed for the computation quite different assumptions have been made in the different formulas, but nevertheless these formulas have all given results which are not widely different if the uncertainty of some of the experimental data are considered. Nevertheless, the formulas do not always give exactly the same values as they should if all the assumptions and data were rigorously correct. The computation of the cohesion from the latent heat of vaporization should give a correct result since the assumptions made here are less radical than in any of the other methods. Now this method generally gives a value for "*a*" lower, in some cases 5 percent lower, than that computed from the critical data. But I have not been able to attach more importance to this deviation for the reason that the computation must be made close to the critical temperature, within a fraction of a degree of it, and a very slight error in the difference of the vapor and liquid densities would make a very large error in "*a*." That the formulas proposed for "*a*" are possibly not entirely accurate may be shown also by the following circumstance: From the formula $a = ((S^2 - S + 2)/(S - 2))P_cV_c^2$ and the formula $a = M((S^2 - S + 2)/(S - 2))RT_c^{2/3}(T_c - T)^{1/3}/(d_1 - d_v)$ we have $V_c^2 = MR(T_c - T)^{1/3}T_c^{2/3}/(d_1 - d_v)P_c$. If now we compute d_c of oxygen by this formula from the densities of liquid and vapor oxygen found by Mathias and Onnes, we find indeed a constant value for d_c, but a density nearly 3 percent higher than that computed by the rectilinear diameter law, as follows:

Table II

Computation of the critical density of oxygen from the densities at different temperatures, *t*

t	d_c
—118.8°	0.4413
—120.4	0.4428
—140.2	0.4437
—154.51	0.4427

d_c computed by Mathias and Onnes by the rectilinear diameter law was 0.4299.

The deviation with pentane was in the opposite direction. d_c was found by S. Young to be 0.2323. If it is calculated by the foregoing method from Young's density figures we have

t	d_c
0°	0.2235
160	0.2265

In this case the result was about 3 percent too low.

With octane the computed and found values agree very well, as follows, using Young's density figures at various temperatures.

t	d_c
0°	0.2319
60	0.2324
120	0.2336
160	0.2348
190	0.2352
230	0.2372

The density values show a tendency to advance. The mean value of about 0.2330 is very close to that determined by Young of 0.2327.

The critical density calculated for various other substances from the liquid and vapor densities resulted as follows when compared with the found values:

Substance	Temperature and density from which calculation made	d_c Calculated	d_c Found
Benzene	0° $d_l = 0.90006$; $d_v = 0.00012$	0.3019	0.3045
Fl-benzene	0° $d_l = 1.04653$	0.3495	0.3541
Br-benzene	0° $d_l = 1.52182$	0.4804	0.4853
CO_2	0° $d_l = 0.914$; $d_v = 0.096$	0.4749	0.46
CCl_4	0° $d_l = 1.63255$	0.5569	0.5576
Ethyl ether	0° $d_l = 0.7362$; $d_v = 0.000827$	0.2605	0.2625
	60° $d_l = 0.66580$; $d_v = 0.006771$	0.2622	

The foregoing figures show that the formula used for the calculation of d_c, which was derived from two of the formulas used in the calculation of "*a*," gives results which agree generally within 1 percent of the values of the critical density determined by experiment, but in some cases there is a deviation of about 3 percent. We may, I think estimate the uncertainty in the value of "*a*" and hence of M^2K, as not more than 2–3 percent.

The formula which I have chosen for the calculation of the value of "*a*" is that which is based on the assumption that the value of b_c is $2V_c/S$. This formula is: $a = ((S^2 - S + 2)/(S - 2))P_cV_c^2$. This equation involves only the critical data and may be applied to the largest number of substances.

While the calculation of the total valence of the molecules is thus subject to these uncertainties, it is probable that the substances are arranged in their proper order of the amount of residual valence and that the error in the total valence of the molecule is not more than 5 percent at the outside. The results are given in Table III. The values of "*a*" are taken from column 4 of Table VIII of my paper[1] on the internal pressures of liquids.

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[1] Mathews: *Loc. cit.*, p. 622.

TABLE III

Amount of residual valence

I Substance	II Formula	III Theoretical No. of valences	IV Total No. of valences by formula $a = C^1(\text{Wt.} \times \text{Val.})^{1/3}$	V Residual valence
Hydrogen	H_2	2	2.195	0.195
Oxygen	O_2	2	2.195	0.195
Nitrogen	N_2	2	2.197	0.197
Nitrous oxide	N_2O	4(?)	6.765	2.765
Ethylene	C_2H_4	12	12.904	0.904
n-Pentane	C_5H_{12}	32	36.59	4.59
i-Pentane	C_5H_{12}	32	35.95	3.95
n-Hexane	C_6H_{14}	38	43.42	5.42
Diisopropyl	C_6H_{14}	38	42.41	4.41
Heptane	C_7H_{16}	44	50.89	6.89
n-Octane	C_8H_{18}	50	59.08	9.08
Diisobutyl	C_8H_{18}	50	56.30	6.30
Ether	$C_4H_{10}O$	28	30.45	2.45
Carbon tetra-chloride	CCl_4	16 (Cl = 3)	20.28	4.28
Benzene	C_6H_6	30	33.70	3.70
Chlor-benzene	C_6H_5Cl	32	36.40	4.40
Methyl formate	$C_2H_4O_2$	16	18.12	2.12
Ethyl formate	$C_3H_6O_2$	22	24.39	2.39
Methyl acetate	$C_3H_6O_2$	22	23.52	1.52
Methyl propionate	$C_4H_8O_2$	28	29.38	1.38
Ethyl acetate	$C_4H_8O_2$	28	29.20	1.20
Propyl formate	$C_4H_8O_2$	28	31.16	3.16
Methyl butyrate	$C_5H_{10}O_2$	34	36.11	2.11
Methyl iso-butyrate	$C_5H_{10}O_2$	34	35.30	1.30
Propyl acetate	$C_5H_{10}O_2$	34	36.05	2.05
Ethyl propionate	$C_5H_{10}O_2$	34	35.80	1.80
Stannic chloride	$SnCl_4$	16 (Cl = 3)	17.68	1.68
Carbon bisulfide	CS_2	16 (S = 6)	15.94*	—
Methane	CH_4	8	8.15	0.15

* "a" computed from the surface tension.

These figures speak for themselves, but a word of comment may be made on some of them. It seems probable from the greater solubility in water of oxygen and nitrogen than hydrogen, that the average residual valence of a molecule

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[1] $C = 3.20 \times 10^{-37} \times N^2$.

of hydrogen gas is somewhat lower than the figures indicate. In the series methane, ethylene, pentane, hexane, heptane and octane the residual valence is, respectively, 0.15, 0.9, 4.6, 5.42, 6.89, 9.05. In other words, the residual valence increases with the number of carbon atoms as Armstrong has already inferred it should do. If 0.15 be considered as the average amount of residual valence of a carbon atom when united with hydrogen and if the amount of residual valence increases proportional to the square of the number of carbon atoms, we should have R. Val. $= n^2\ 0.15$, n being the number of carbon atoms. By this formula the number of residual valences in the series mentioned should be, respectively, 0.6 for ethylene, 3.75 for pentane, 5.40 for hexane, 7.35 for heptane, and 9.60 for octane. These values are not very different from those actually found. This relationship does not hold for the esters.

Another fact may be noticed, namely, that the differences between the total number of valences in the various groups of esters is very nearly the theoretical number. Thus between methyl formate and methyl acetate a difference of six valences is required. 5.40 was the difference found. If we take the average of the total number of valences found in the two esters of the formula $C_3H_6O_2$ it is 23.95. This is 5.75 valences more than methyl formate has and is almost exactly six less than the next higher homologues of the formula $C_4H_8O_2$, of which the average number of valences found was 29.91. This in its turn is again 5.79 (required 6) valences less than the average of the next higher group of the formula $C_5H_{10}O_2$. Theoretically, there should be a difference of 32 valences between the molecule of hydrogen and a molecule of the formula $C_5H_{10}O_2$, whereas the method actually shows a difference of 33.62. It is certainly reasonable to suppose that this difference from the theoretical is to be ascribed to the larger amount of residual valence possessed on the average by a molecule of the ester as compared with hydrogen.

In the case of the chlorine compounds I have assumed that the valence of chlorine is three. The reason for this is that I have not been able to find any chlorine compounds which show chlorine to have a lower valence than this. It might be assumed that these three valences were composed of one chief and two residual valences. In that case one should, of course, make the residual valence of chlor-benzene 6.40 instead of the value 4.40 which I have indicated. Another reason why I have not counted these two valences of chlorine as residual valences is that these chlorine compounds are non-associating compounds, or at any rate they associate very little. Hence the valences, sixteen in number, found in carbon tetra-chloride are probably not free residual valences, in the sense that they are valences in an active form but not saturated in the molecule, but they must be saturated in the molecule. On the other hand, the excess of 4.28 valences found above the calculated amount may or may not be in part saturated within the molecule.

It is evident then that the determination of the residual valence by this method of subtracting the theoretical number from the total number found is open to these serious sources of uncertainty. All that can be claimed for the method at this time is that it gives a method of calculating the total valences and thus estimating the residual valence, and that so far as indications go in the hydrocarbons and the esters the compounds are at least arranged in the order in which they would be placed, judging from their reactions, if arranged according to the amount of residual valence they possess. I hope that methods will be found to differentiate more clearly between the valences extending between the atoms and those additional valences extending outward from the atoms making the residual valence proper.

It is still too early to attempt to correlate the amount of residual valence with the solubility of compounds. It is at least possible that in solubility other factors than the number of valences come into play. The attraction between the molecules of solvent and solute may involve the factors which have been shown to influence cohesion, namely, molecular weight and number of valences, as well as the amount of residual valence; it may also involve, of course, the amount of dissociation of the aggregates formed by cohesion or residual valence. It is probable, since the atomic unions are as a rule far more stable than the cohesive, the chemical attraction between the atoms being of an electro-static kind, that the union between solvent and solute due to the residual valence is of far more importance than that of a cohesional nature, just as the cohesional attraction is of vastly greater importance than the gravitational attraction; and there are not lacking indications that residual valence plays a very important part in solubility. I may mention in this connection the series helium to xenon already discussed elsewhere; the great dissolving power of associated as contrasted with non-associated liquids, shown by the solvent powers of water; the less association of associating substances when dissolved in associating solvents as compared with their state in non-associating solvents; the greater solubility of such gases as hydrogen sulphide, ammonia, sulphur dioxide which have greater residual valence than nitrogen, hydrogen and oxygen, and the fact that they are known to combine with water, and so on.

The residual valence is hardly ever found to be a whole number. The probable explanation of this is that the number found represents only the average amount of residual valence possessed by the molecules. It is probable that the residual valences open up in pairs, one positive and one negative, but that at any instant of time only a few molecules have them open, so that the average amount possessed by each molecule may appear to be a fraction.

Summary

The amount of residual valence of a number of non-associating liquids and gases has been computed by subtracting from the total number of valences which the molecule possesses, as shown by its cohesion, the number which there is reason to believe extend between the atoms of the molecule. The difference is considered to be the residual valence.

The computation of the total number of valences in a molecule from the cohesion is made from van der Waals' factor "a" by the formula: $a = C(\text{Mol. Wt.} \times \text{Val. number})^{1/2}$. a was computed by the formula already given, namely $a = ((S^2 - S + 2)/(S - 2))P_cV_c^2$, in which S is the critical coefficient and P_c and V_c the critical pressure and volume. The constant C for a single pair of molecules was assumed to be equal to $(m^2k)^{1/2}$, in which m is the gravitational mass of a molecule of unity molecular weight and k the gravitational constant. From Millikan's recent determination of the number, N, of molecules in a gram mol, the value of this constant was 3.2015×10^{-37} expressed in dynes. For a gram mol C is 1.177×10^{11}.

Owing to various uncertainties and assumptions in the calculations, this method of determination can be regarded only as of the nature of an approximation to the actual amount of residual valence of molecules.

ELECTROLYTIC DEPOSITION OF BRASS ON A ROTATING CATHODE

BY C. W. BENNETT AND A. W. DAVISON

In a previous paper[1] a study was made of the relation between tensile strength of electrolytic copper and speed of rotation of the cathode. The results obtained were highly satisfactory, and pointed to possibilities of wider application of the process, in enhancing the physical properties, and increasing the tensile strength of brass and other electrolytically deposited alloys, the unsatisfactory nature of which has long been deplored.[2] In the paper referred to above, some work was reported on the copper-zinc and the copper-tin alloys, but the time at hand was inadequate for an exhaustive study of the question, and this paper is the result of further work along these lines.

It was decided at first to discard the cyanide solution, because of the entirely unsatisfactory results which are obtained from it, and to search for some other solution or combination of solutions which might give a less brittle and more coherent deposit.

In order to secure the simultaneous precipitation of two metals from the same solution, the single potentials of those metals in that solution must be very close together, or else marked impoverishment must take place. Single potential measurements on solutions of the double cyanides clearly show that the curves are not necessarily coincident, but they are almost parallel and are reasonably close together. Their distance apart will depend to a certain extent on the amount of free potassium cyanide present. A brass is probably deposited from a solution of the mixed cyanides by reason of impoverishment. Reasoning from conditions in this solution, where a brass is known to deposit, to those which must

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[1] Bennett: Jour. Phys. Chem., 16, 294 (1912).

[2] Field: The Electrician, 63, 632 (1909).

obtain in any other solution from which a brass would deposit, it is seen that the curves representing single potentials at various current densities must first of all be nearly parallel, and must also be nearly equal in magnitude. In order to determine what salts might be expected to give brass, such curves were highly desirable.

The electrochemical literature is filled with measurements of single potentials for the various metals in solutions of their salts, referred to the standard calomel electrode, but these values are all taken against stationary electrodes. With the rotating cathode, in the case of one of the metals under consideration, it has been shown[1] that marked concentration changes, accompanied by increase in potential, take place, and it was deemed desirable to measure the single potentials under conditions as near as possible to those under which precipitation would take place, in other words, with the cathode rotating at its normal speed, and with full current flowing. Under such conditions, of course, a brass cathode could not be realized in the measurements. Bancroft[2] has pointed out that an alloy should show the potential of its less noble phase, and Spitzer[3] has shown that electrolytic brass deviates from this but slightly. Since the measurements for the purpose at hand would be but relative, the form rather than the absolute value of the curve being desired, the fact that a brass cathode could not be maintained during the measurements is unimportant.

As previously stated, the calomel electrode is used in the majority of single potential measurements. In this instance, however, it was found difficult to keep the calomel electrode at constant distance from the cathode, for the latter was belt-driven, and its position in the cell would vary from one run to another. Fastening the calomel electrode to the cathode frame in order to secure a constant separation from the cathode

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[1] Bennett and Brown: Jour. Phys. Chem., 17, 373 (1913); Am. Electrochem. Soc., 23, 383 (1913).

[2] Bancroft: Am. Electrochem. Soc., 3, 297 (1909).

[3] Spitzer: Zeit. Elektrochemie, 11, 345 (1909).

was impossible for mechanical reasons, hence a platinum electrode, which could be fastened to the frame of the apparatus, was substituted. This consisted of a piece of platinum wire one millimeter in diameter and twenty-five centimeters long, held firmly at a fixed distance of one centimeter from the cathode, by means of a fiber strip.

The actual measurement is therefore the voltage drop between a platinum anode and a copper or zinc cathode, respectively, in the solutions used. The anode voltage will be practically constant no matter whether the solution be one of copper or of zinc salt; for the platinum adsorbs practically a constant amount of oxygen. It was necessary to have the conditions such that the platinum was anode for some time before the measurement was made, so that sufficient time was allowed for the adsorption of the maximum amount of oxygen. So that, while the results are probably not so accurate as if a calomel electrode had been used, they represent values which do not differ from the true ones by a large amount. It may be considered, therefore, that the potential of the platinum anode is practically constant in all the measurements, and that the change in voltage is due to other conditions, such as cathode voltage, concentration differences, and the resistance of the solution.

As in the previous work, an aluminum cathode was used, since it embodies lightness with ease of stripping off the deposit, when physical tests were to be made. In design it is similar to the one previously described,[1] although since much smaller current densities were here used, the parts are proportionally smaller, and the water-cooled bearing was dispensed with. The cathodes proper were constructed from aluminum pipe 2.7 centimeters outside diameter, and 14.2 centimeters long. Several of these were made, to facilitate the work. At the top they were tapped to take a tapering brass plug, which securely fastens them to the remainder of the rotating parts, consisting of the threaded plug, a steel

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[1] Bennett: Jour. Phys. Chem., 16, 287 (1912).

spindle 1 centimeter in diameter and 15 centimeters long, an aluminum belt wheel, and a brass commutator ring. The bearings, two in number, were brass, 1.5 centimeters long, being lubricated by vaseline, supplied from ordinary grease cups. Current was taken off the commutator ring by means of two graphite brushes 1.2 centimeters in diameter, held in fiber by means of coiled springs. The device was driven from a one-eighth horsepower induction motor, at the rate of 4500 revolutions per minute, although, if desired, other speeds could be obtained by means of different sized pulleys.

Since aluminum is readily attacked by many of the solutions used, it was found necessary to protect the cathode by means of a coating of copper. This was readily applied in an acid copper sulphate bath, with a current density of 25 amperes per square decimeter, the cathode being rotated. When it was desired to remove a deposit from the cathode this layer of copper was stripped off with the brass, and afterward removed from the brass by filing or scraping.

The arrangement of the apparatus is shown in Fig. 1.

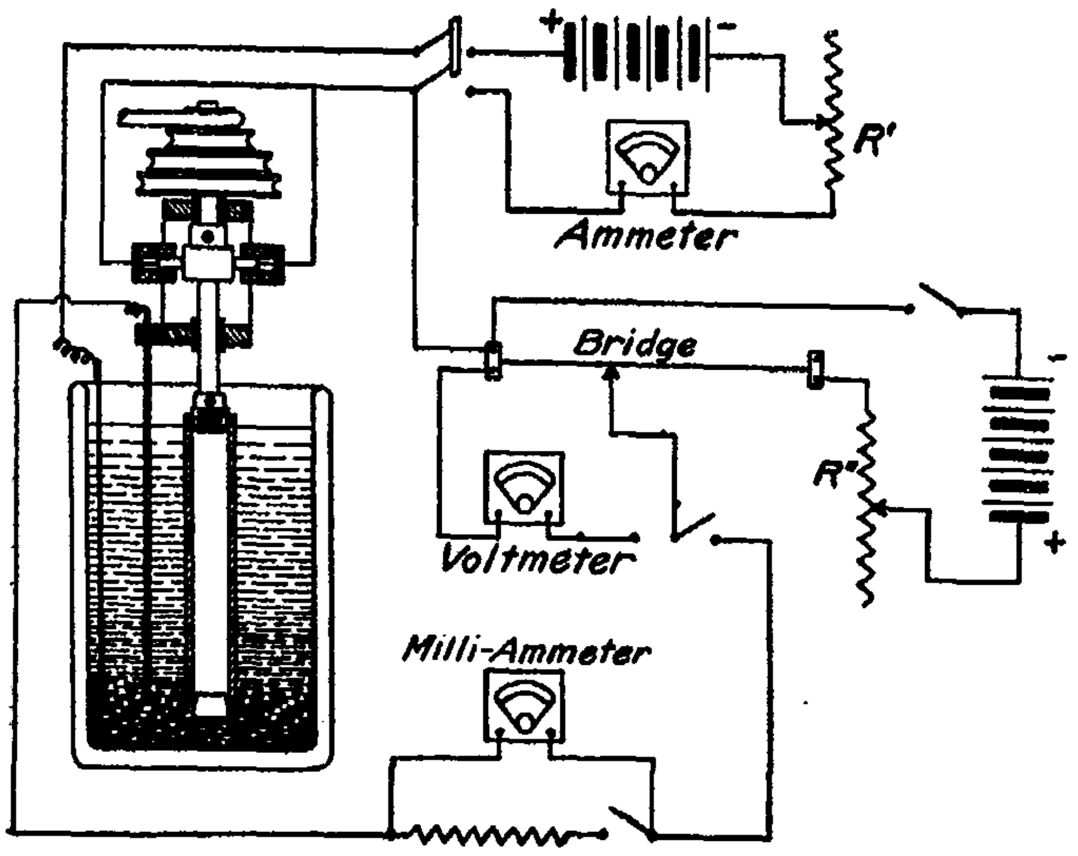

Fig. 1

The current for electrolysis, obtained from either a 28 volt 100 ampere hour lead battery, or from the 110 volt mains, was led in through one side of the double-throw switch directly to the anode, and from the cathode through the other side of the double-throw switch to the ammeter and then to the adjustable resistance. The cathode was also connected to the negative end of a bridge wire, and the platinum electrode was connected through a milliammeter to the movable contact on the bridge. This bridge was in the circuit of a 6 volt Edison set, so that the single potentials were balanced against the drop across the bridge, and this drop measured by throwing the movable contact into circuit with a high resistance voltmeter by means of a double-throw switch. Since only relative values that would be consistent among themselves were required, the objection that the voltmeter does not measure the actual drop at the instant of balancing is overcome. The milliammeter was used in place of a galvanometer because commutation troubles at the cathode with high current densities would cause the galvanometer to go off the scale. Some difficulty was encountered at the commutator due to thermo currents, and consequent electromotive forces, but by allowing the cathode to run until the maximum temperature was reached at the commutator each time before measurements were made, that was eliminated.

The cell consisted of a 1.5 liter glazed porcelain battery jar, and the anodes were of uniform size, 12.5 × 5 × 0.1 cm. The runs were made at 25 degrees centigrade.

The potentials for copper solutions are given in Table I.

The potentials of zinc solutions are given in Table II.

With current flowing, the potentials represent several factors: the potential of the cell oxygen-solution-copper or oxygen-solution-zinc, the drop across the commutator, and the drop across the solution. The last named could have been eliminated only by placing the platinum wire at an infinitesimal distance from the cathode, where the strong agitation would have immediately bent it away.

TABLE I

Potentials of copper in copper salts

Current density, amperes per square decimeter	15% copper sulphate, neutral	15% copper sulphate, 5% sulphuric acid	15% copper sulphate, 10% sulphuric acid	8% copper sulphate, neutral	8% copper sulphate, 5% sulphuric acid	8% copper sulphate, 10% sulphuric acid	8% copper ammonium sulphate, neutral	8% copper ammonium sulphate, 10% sulphuric acid	8% copper ammonium chloride, neutral	8% copper ammonium chloride + 5% hydrochloric acid	8% copper formate, neutral	8% copper formate + 2% formic acid	Copper fluoride saturated	8% copper fluosilicate	7% potassium cuprocyanide
5.0	—	—	—	—	—	—	1.50	1.14	—	—	—	—	—	—	—
4.5	—	—	—	—	—	—	1.30	1.08	—	0.95	—	—	—	—	—
4.0	—	—	—	—	—	—	1.22	0.98	—	0.86	—	—	—	—	—
3.5	—	—	—	—	—	—	1.17	0.92	—	0.80	—	—	3.40	—	—
3.0	1.34	0.74	0.55	—	—	—	1.12	0.88	—	0.73	—	—	3.10	4.80	1.63
2.5	1.15	0.71	0.52	—	—	—	0.97	0.80	0.84	0.68	—	—	2.78	4.40	1.55
2.0	0.97	0.64	0.49	2.25	0.58	0.58	0.85	0.75	0.77	0.63	3.40	3.30	2.47	3.80	1.45
1.5	0.84	0.57	—	1.85	0.55	0.53	0.75	0.69	—	—	2.50	2.40	2.19	3.30	1.35
1.0	0.64	0.50	0.41	1.53	0.51	0.50	0.60	0.60	0.55	0.51	1.67	1.70	1.90	2.50	1.16
0.7	0.53	—	—	1.27	0.48	0.45	0.52	0.55	0.44	0.43	1.26	—	—	—	1.03
0.5	0.44	0.40	0.37	1.03	0.45	0.43	0.45	0.52	0.40	0.38	0.98	0.96	1.57	1.48	0.92
0.3	0.30	0.35	0.35	0.81	0.43	0.42	0.35	0.49	0.35	0.34	0.70	0.62	1.35	0.95	0.83
0.1	0.25	0.28	0.31	0.61	0.40	0.39	0.26	—	—	—	0.42	0.33	1.03	0.52	0.71

TABLE II
Potentials of zinc in zinc salts

Current density in amperes per square decimeter	8% zinc sulphate, neutral	8% zinc ammonium chloride, neutral	8% zinc ammonium chloride + 1% hydrochloric acid	8% zinc ammonium chloride + 2% hydrochloric acid	8% zinc ammonium sulphate, neutral	8% zinc ammonium sulphate + 1% sulphuric acid	8% zinc ammonium sulphate + 2% sulphuric acid	4% potassium zincate	4% potassium zincate + 2% potassium hydroxide	Zinc fluoride, saturated	8% zinc benzene sulphonate	8% zinc fluosilicate	5.25% potassium zinc cyanide
4.0	—	—	—	—	—	2.72	2.49	—	—	4.20	—	—	—
3.5	3.50	—	—	—	2.95	2.43	2.38	2.35	—	4.00	4.50	—	—
3.0	3.20	—	—	—	2.57	2.27	2.08	2.11	2.32	3.80	4.20	—	—
2.5	2.93	—	—	—	2.43	2.03	2.02	1.93	2.06	3.60	3.80	4.80	—
2.0	2.55	1.95	1.53	1.39	2.30	1.95	1.88	1.81	1.91	3.40	3.50	4.30	1.76
1.5	2.20	1.57	1.34	1.31	2.12	1.83	1.69	1.73	1.81	3.10	3.20	3.70	1.68
1.0	1.90	1.48	1.26	1.26	1.75	1.71	1.51	1.66	1.68	2.75	2.85	2.90	1.64
0.7	1.67	1.45	1.20	1.18	1.60	1.56	1.36	1.58	1.58	—	—	—	1.53
0.5	1.51	1.39	1.16	1.15	1.48	1.47	1.26	1.55	1.52	2.33	2.41	1.85	1.41
0.3	1.33	1.30	1.12	1.10	1.41	1.40	1.18	1.51	1.47	2.06	2.29	1.39	—
0.1	1.23	1.22	—	—	1.28	1.15	—	1.41	1.39	1.68	2.11	1.20	—

Cupric ammonium chloride cannot be used in plating baths because of the formation of a heavy flocculent precipitate, which is doubtless cuprous chloride. Single potentials of this salt were measured, however, and the curve was plotted, in order to give some idea of the potential. The deposit in the case of zinc ammonium chloride was worthless, and the same is true of the one obtained from neutral copper formate.

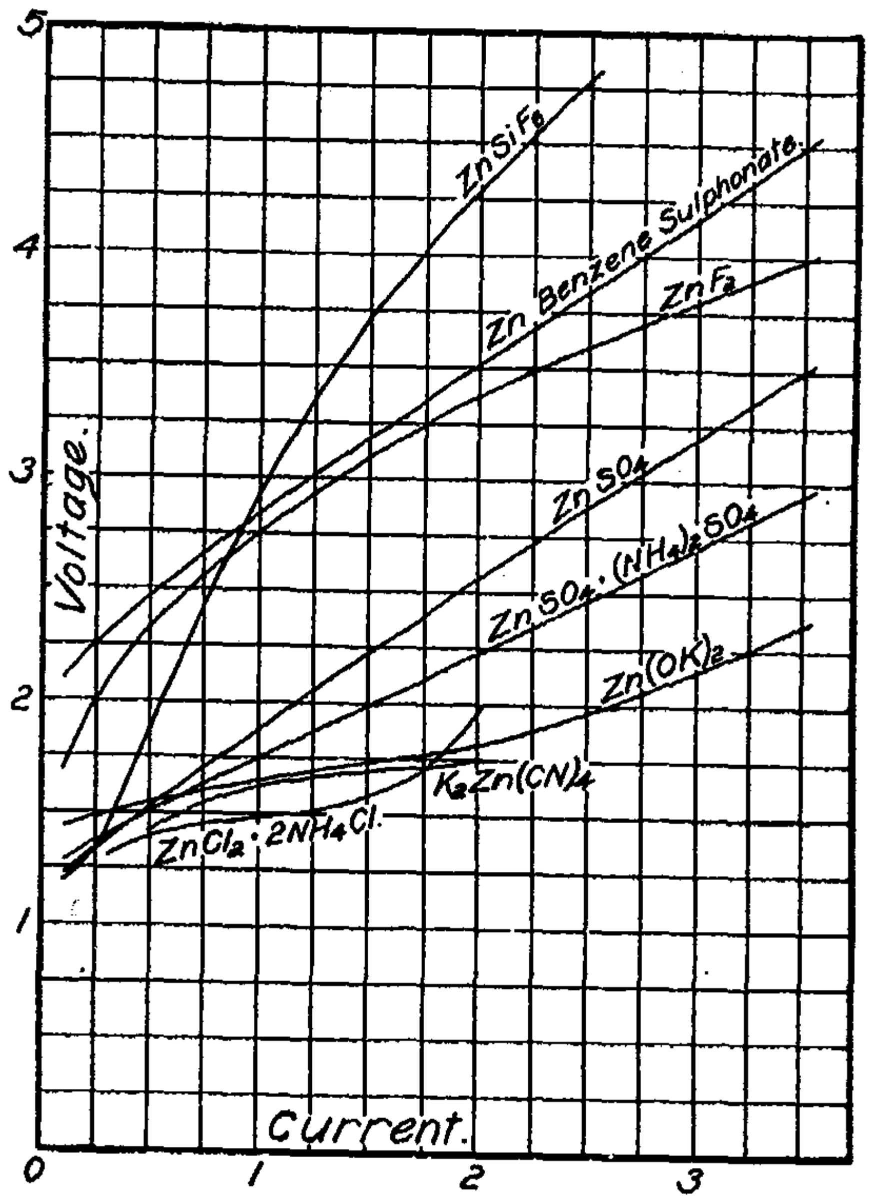

Fig. 2

With copper benzene sulphonate the deposit was of a doubtful value, and potential measurements were impossible because the platinum wire at once became covered with a black layer of copper when it was placed in the solution.

In all the other cases recorded, good deposits of the metal were obtained, and it was assumed that they were capable of further exploitation.

In plotting these curves representing single potential against current density, for the sake of simplicity, the zinc salts were plotted on one sheet and the copper ones upon a separate one, Figs. 2 and 3.

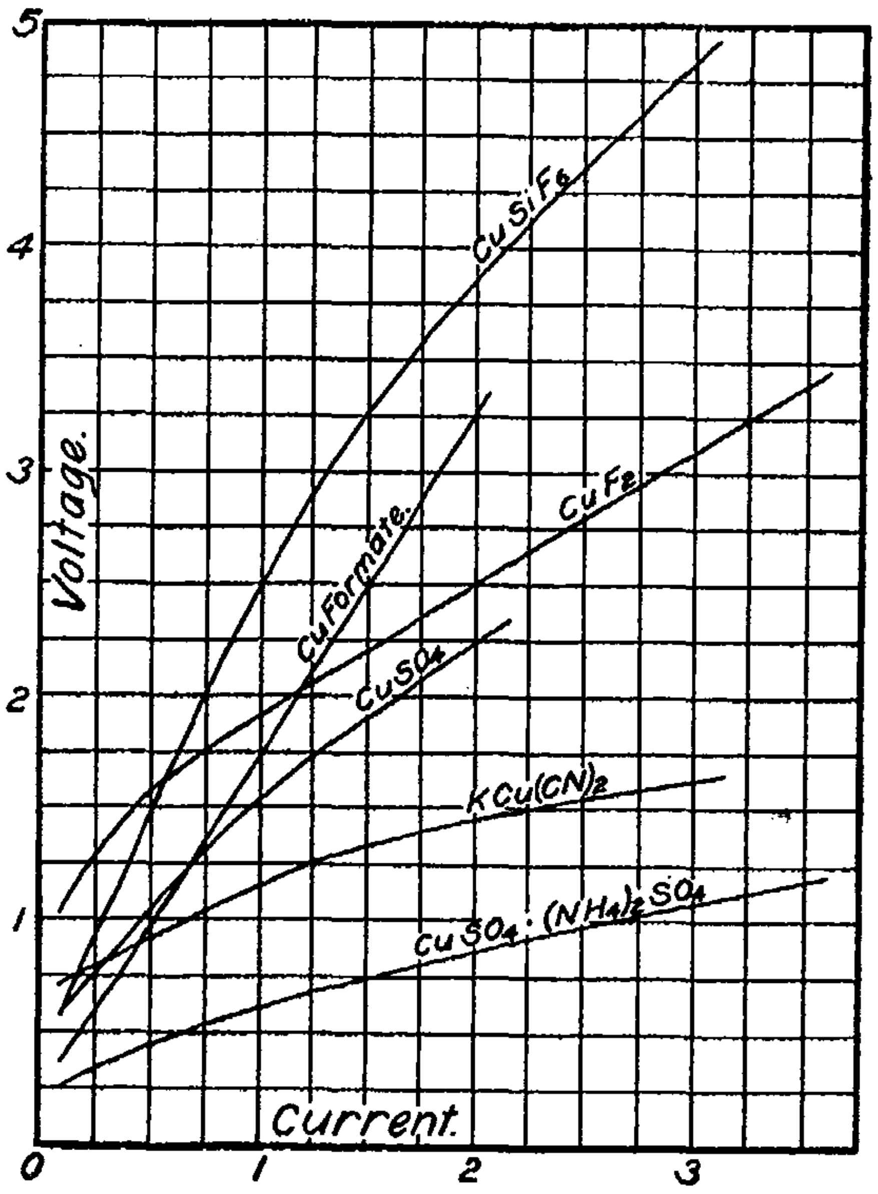

Fig. 3

A consideration of the curves shows that the pairs of similar form, and of comparable magnitude, are the following:

1. Copper sulphate and zinc sulphate.
2. Copper fluosilicate and zinc benzene sulphonate.
3. Copper benzene sulphonate and zinc sulphate.

4. Copper fluosilicate and zinc fluosilicate.
5. Copper fluoride and zinc fluoride.
6. Copper fluoride and zinc sulphate.
7. Copper ammonium sulphate and zinc ammonium sulphate.

The results of the individual runs are as follows:

It was certainly not to be expected that a brass could be deposited from a solution of the mixed sulphates, since it is the one employed in the quantitative separation of these metals in the determination of copper. A good deposit cannot be obtained from neutral solution; acidification introduces an ion whose potential is between those of the two metals, and hence simultaneous deposition of the metals is impossible.[1]

Above a current density of 1 ampere per square decimeter the curves for copper fluosilicate and zinc benzene sulphonate come the nearest of all to coincidence, the potentials being but a small fraction of a volt apart. But when one considers that a solution of the two salts will contain molecules of the four compounds, copper fluosilicate, copper benzene sulphonate, zinc fluosilicate, and zinc benzene sulphonate, it is quite apparent that the metal which will be precipitated will be the one having the salt of the lowest single potential; in this case, copper from benzene sulphonate. Experiment showed that under all conditions of current density and concentration, except where the copper concentration was slight and the zinc deposit bad, copper was deposited or else was accompanied by a worthless deposit of zinc.

Copper benzene sulphonate and zinc sulphate can be dismissed with very little comment, for copper sulphate is formed in the bath, and since it possesses a much lower potential than any of the other salts present, copper alone is deposited.

With copper and zinc fluosilicates the potential of zinc is uniformly higher than that of copper, although the difference is not so great as in many other instances. It was

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[1] Field: The Electrician, 63, 632 (1909).

thought that by starting with a zinc solution, and running the cell with a copper anode, a point would finally be reached where the concentration of both salts would be right for the deposition of brass. Should such a point be reached, a brass anode of the desired composition could be substituted and, barring difficulties of corrosion, the brass should continue to deposit. Accordingly, a solution containing 8 percent zinc fluosilicate was prepared, and electrolyzed with an anode and cathode current density of 5 amperes per square decimeter with a copper anode until the copper content was high enough to give copper at the cathode. This deposit was worthless, due it was thought to too high a current density. A zinc anode was then substituted, and the cell run with a current density of one ampere per square decimeter until zinc began to deposit again. This procedure was carried out repeatedly, with current densities of from 0.1 to 10 amperes per square decimeter, but in no case was a brass observed. The deposit, too, was worthless, tending to grow out in flakey masses, and to fall off. The zinc would be a dirty black, and the copper a sickly looking red. Addition of 12 percent free fluosilicic acid did not improve the deposit.

Just at the point where the cell seemed to change from depositing zinc to copper, a brass anode was put in, and electrolysis continued with a current density of 1 ampere per square decimeter for three hours in order to determine under what conditions the metals were being deposited at that concentration of solution. A black incoherent deposit was found on the lower half of the cathode, and a bad copper deposit above this where the air was stirred down by the cathode. After the run was stopped, a mass of finely divided zinc settled to the bottom of the cell. This peculiar segregation of the deposit was undoubtedly due to the fact that bad zinc and copper were being deposited together over the cathode, but that the color of zinc was predominant. At the top, where surging of air bubbles took place, the zinc was partly oxidized, and knocked off, leaving the copper on the cathode. The actual amount of copper in the solution when that metal would deposit was always small, because rapid agitation prevented excessive impoverishment.

A few experiments made on this same solution with stationary electrodes failed to show any deposit of brass. Much smaller current densities were used, ranging from 0.1 to 1.0 ampere per square decimeter. The conditions of deposition were very much the same as with the rotating cathode, except that a great deal more copper was required in the solution before that metal would precipitate in any large percent. This was no doubt occasioned by impoverishment of copper at the cathode, which permitted slimy zinc to deposit.

In this case the metals are too far apart in potential, for when the composition of the bath is right for their precipitation in the ratio required for brass, none results.

The curves for the mixed fluorides certainly do not indicate that a brass can be deposited from these solutions, and tests similar to those of the preceding instances failed to give any at all.

Copper fluoride and zinc sulphate seem to give curves that are quite similar in form, and a number of experiments were made on these solutions. A brass could not be deposited at any current density, under any conditions of concentration. This case is entirely analogous to the one of copper fluosilicate and zinc benzene sulphonate, in that double decomposition results in the formation of copper sulphate, copper fluoride, zinc sulphate, and zinc fluoride, and when these salts are present in the bath together, copper alone is deposited from the sulphate.

The curves for the double ammonium sulphates are so far apart that results could not be obtained from them.

In addition to those salts for which single potentials were measured, a few runs were made on molecular solutions of the mixed chlorides, using 5 percent sodium chloride to insure quantitative solution at the anode. Starting with a zinc solution, and using a copper anode, the latter metal would dissolve in the zinc chloride as cuprous chloride.

Various concentrations of copper, up to the point where cuprous chloride would slime at the anode, were tried, but no brass was obtained, although it was possible to get the zinc and copper precipitating at the same time under conditions which were not noted, because the copper would not stick to the cathode, but was thrown around in the solution, settling out after the run was stopped.

Hydrolysis of the zinc, with precipitation of white zinc hydroxide, bothered to a great extent in this solution also.

The general nature of the deposit indicated that perhaps the solution was too concentrated, and another run was made, using a normal solution, 2 percent sodium chloride, and 5 percent hydrochloric acid added to drive back hydrolysis of the zinc. Careful variation of current density and metal ratio failed to show any brass deposit, the character of the deposit being much the same as for the more concentrated solution.

A general survey of the more common salts, and those, cyanides excepted, which give good and indifferent deposits from single solutions therefore results in failure to find a satisfactory solution for depositing brass. Brasses obtained from the cyanide solutions are known to be unsatisfactory, from the physical standpoint.[1] It was therefore deemed advisable to investigate the causes of this undesirable property, and to remedy it if possible. A number of runs was therefore made with cyanide solutions, the results of which follow.

In preparing the solutions, copper or zinc sulphate in solution was treated with an amount of potassium cyanide equivalent for the formation of the simple single cyanide, and the precipitate filtered out and washed free from sulphates. It was then dissolved hot by treatment with sufficient potassium cyanide solution to give the double cyanide plus one molecule of free potassium cyanide, that amount being necessary in order to secure quantitative solution of the anode. There is, however, the disadvantage that strong

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[1] Bennett: Jour. Phys. Chem., 16, 294 (1912). Field: Electrican, loc. cit.

hydrogen evolution takes place with increasing cyanide concentration.[1]

By preparing solutions of both potassium cuprocyanide and potassium zinc cyanide in this manner, and mixing them, it was possible to vary the metal content very easily. The method of "working one metal into the bath," much used by practical platers, was quite frequently resorted to also. When a solution was depositing a brass satisfactorily, analyses were made for copper, zinc, and free potassium cyanide. The copper was determined by the usual electrolytic method of converting to sulphate by "fuming down" 25 cubic centimeters of sample with 10 cubic centimeters of concentrated sulphuric acid, diluting to 500 cubic centimeters, neutralizing with ammonia, then adding 10 cubic centimeters of sulphuric acid and electrolyzing with platinum flag anodes and rotating copper cathodes. Zinc was then determined from this same solution, by the pyrophosphate method, as modified by Findlay and Cummeley.[2] The nickel method of Lundell,[3] which gives free alkali cyanides in the presence of copper and zinc, was employed in determining free potassium cyanide.

The brasses were analyzed by the same scheme, after having been dissolved in nitric acid.

For carbon and hydrogen in the brass, an ordinary electric combustion oven, heated to 900 degrees, was employed; using for the oxidizing agent air previously bubbled through 2 : 1 potassium hydroxide, and concentrated sulphuric acid. Water from oxidation of hydrogen was collected in concentrated sulphuric acid, and carbon dioxide in 2 : 1 potassium hydroxide followed by concentrated sulphuric acid.

The samples were also polished, etched with 1 : 3 ammonia, and photomicrographs were taken, to get at their structure and general appearance.

The procedure in the first run was to start with a molecular solution of copper double cyanide, containing one mole-

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[1] Field: loc. cit. Spitzer: loc. cit.

[2] Jour. Chem. Soc., 103, 1104 (1913).

[3] Am. Electrochem. Soc., 25 (1914).

cule free potassium cyanide, and to run with a zinc anode until brass appeared at the cathode. The current density was 3 amperes per square decimeter. When the cathode was first examined, the deposit seemed to be nearly all zinc, showing that the concentration of zinc necessary to give a brass had been exceeded, hence a copper anode was substituted and the deposit watched more closely until the brass reappeared. Then a brass anode, copper 70 percent, zinc 30 percent, was put in and the cell run until a deposit one millimeter in thickness had formed on the cathode. This brass was very brittle, non-homogeneous, and extremely hard, hence no analyses were made of it, or of the solution.

The second run, 25 hours with a current density of 3 amperes per square decimeter, was discontinued because the brass proved to be extremely brittle.

The cyanide content in the third run was quite high, probably about 50 grams per liter, so that appreciable solution of the cathode took place, and holes developed in the copper coating of the cathode which permitted the solution to attack the aluminum.

The fourth run was made with a current density of 3 amperes per square decimeter for 58 hours. 95 grams of brass were deposited with an efficiency of 53 percent. The metal contained 71.5 percent of copper and 27.7 percent zinc; 0.07 percent carbon, and 36 volumes of hydrogen. The carbon may come from colloidal carbon precipitated with the metal, from occluded cyanogen, or from potassium cyanide mechanically enclosed in the particles. The last possibility is doubtless the case, because the odor of hydrocyanic acid was very pronounced when the sample was dissolved. If the carbon be calculated in terms of potassium cyanide, it gives a value of 0.28 percent, and the analysis totals up 99.65 percent. The composition of the bath was:

	Grams per liter
Copper	50.8
Zinc	7.1
Free potassium cyanide	30.0

The metal was extremely hard and very brittle. It resembled in appearance and color ordinary cast brass of the same composition. The photomicrograph, Fig. 4, shows a very peculiar construction, definite crystal form evidently being entirely lacking. The structure was wartlike with small canals running in every direction throughout the mass. These may be attributed to the impurities in the metal.

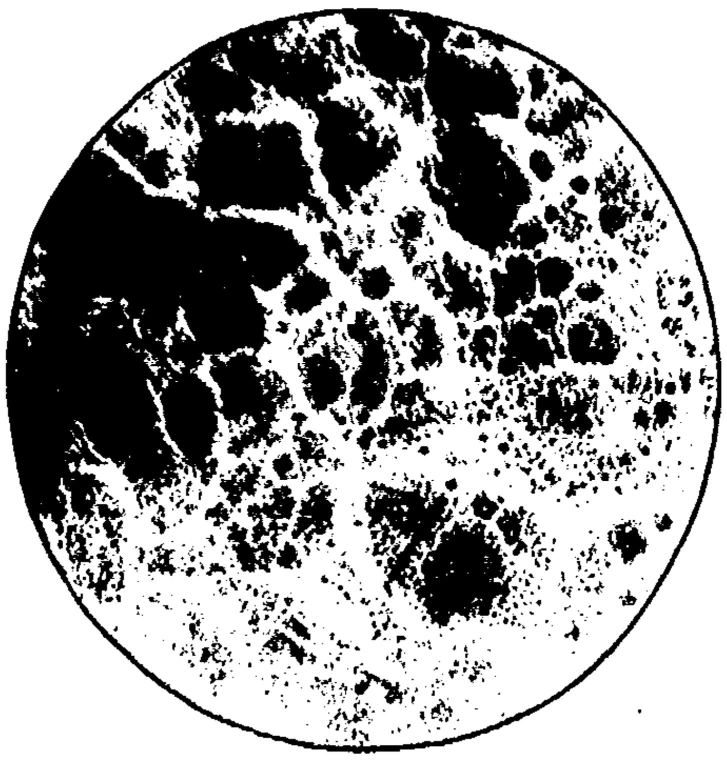

Fig. 4

A sample, Fig. 5, was boiled for two hours in tenth normal potassium hydroxide[1] for the purpose of removing hydrogen. This was much more homogeneous, the canals were almost entirely removed, and the crystals were much smaller. The tensile strength was increased somewhat by this treatment, but not enough to warrant physical tests. Annealing at this point would have undoubtedly increased the tensile strengths immensely, but that procedure is outside the province of this paper.

In order to cut down the amount of hydrogen present in the deposit, a higher temperature was desirable; hence the next run was carried on at 80 degrees, the cell being heated

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[1] Johnson: Proc. Roy. Soc., 23, 174 (1875).

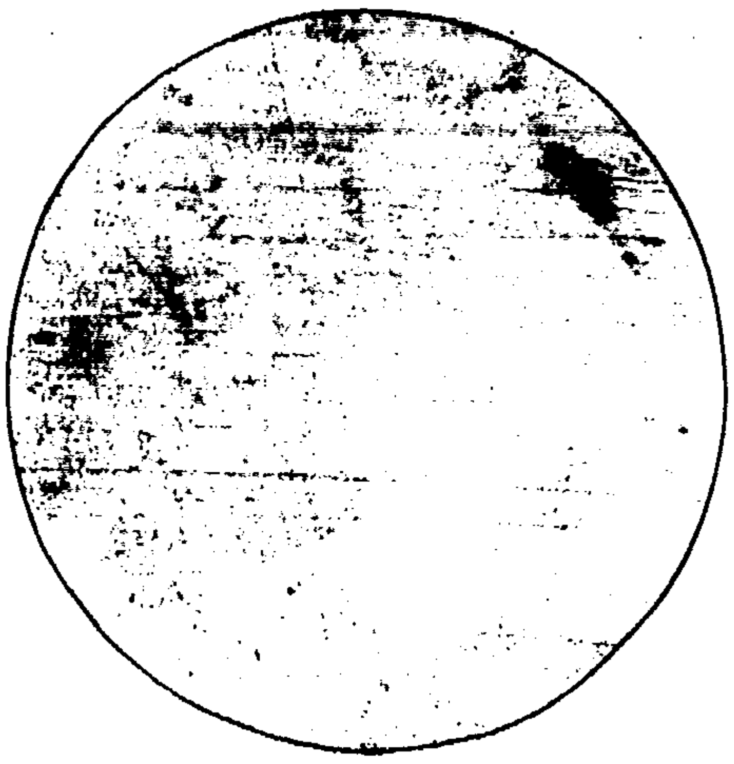

Fig. 5

by means of an electric hot plate. Water was added from time to time in order to keep the volume of the solution constant. The preceding solution was used, after having had its metal content adjusted by alternately running with zinc, then with copper electrodes, until the brass was of the desired composition. The current density could be raised to 4.7 amperes at this temperature, and the deposit was obtained with higher efficiency. The resulting brass was extremely hard and very brittle, but less brittle than the preceding samples. The photomicrograph, Fig. 6, shows that the deposit is more compact, but it was not satisfactory. The hydrogen in the sample ran 10.2 volumes, and the carbon 0.08 percent. Thus heating the bath lowers the amount of hydrogen, but does not tend to change the amount of carbon to any marked degree. The metal content of the deposit was, copper, 70.4, and zinc, 28.7 percent. A photomicrograph, Fig. 7, taken on a plane perpendicular to the axis of the cathode showed marked striations throughout the deposit, caused by variations in the composition of the bath due to evaporation and subsequent replacement of water. Temperature variations of plus or minus 5 degrees also took place, and that would change the metal ratio of the deposit. Removal of the cathode for inspection may also have caused faults in the deposit.

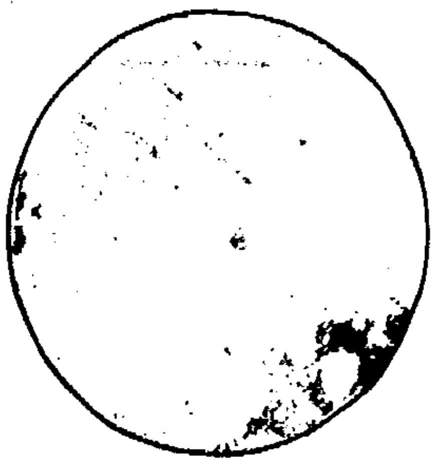

Fig. 6

Fig. 7

In order to ascertain to some extent the effects of concentration in the next run, the concentration of the components of the bath was reduced, and after the usual thickness of brass was deposited, analysis showed the following composition of the bath:

	Grams per liter
Copper	25.8
Zinc	3.4
Free potassium cyanide	36.0

This is what one would predict in a cell where rapid circulation of the electrolyte is being maintained, since increasing the amount of free cyanide increases the potential of copper more than that of zinc,[1] and as the potentials become farther and farther apart, the concentration of the more noble metal must decrease faster than that of the less noble one. The presence of carbon and cyanogen in the samples, leads to the supposition that these impurities come from the free potassium cyanide in the solution. The presence of this substance serves two purposes: first, it insures quantitative solution of the anode; and second, it brings the decomposition potentials of copper and zinc nearer together. These two

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[1] Thompson: loc. cit. Spitzer: loc. cit.

results can be accomplished in a slightly different way, and it was decided to eliminate the free cyanide to see if some of the bad effects could not be eliminated. The solution of the anode can be forced by the addition of a small amount of a soluble chloride or a sulphate, for instance, sodium chloride or sodium sulphate. Consequently, the decomposition potentials of the two metals may be more or less taken care of by concentration differences; that is, the concentration of the one salt can be made very low, while the concentration of the other one is relatively high. It was therefore decided to make an experiment with practically no free cyanide in the solution in which sodium chloride was added to ensure the solution of the anode.

With the free potassium cyanide content reduced to a minimum, and with 1 per cent sodium chloride in the solution, a bath, whose metal composition was not determined, gives a brass at current densities as high as 5 amperes per square decimeter, when run at 25 degrees, but the deposit is just as brittle as before. If the temperature be raised to 80 degrees, cuprous chloride gradually forms, and the deposit consists largely of slimy zinc.

When 1 percent sodium sulphate is added to a solution of the double cyanides containing no free cyanide, the anode dissolves satisfactorily, but the deposit is quite analogous to those obtained in the previous instances. Analysis of a bath which had been depositing brass for some time showed approximately 30 grams of copper and 20 grams of zinc per liter. After this cell had been running for some hours, the deposit at the top of the cathode became high in zinc, while that lower down was normal. This was caused by oxidation, for when the cell was run with illuminating gas above the solution, brass was deposited throughout the entire immersed area.

The usual brass plate that is applied to objects in a stationary bath, or by the "barrel method," conforms to the trade requirements of hardness and beauty, so that it is an admirable protecting agent. It is possible to give it a very high polish, but its hardness must not be confused with true tensile strength. If one allows a stationary deposit to build up until a thickness of several millimeters be attained, and then strips it off the cathode, it is found that it can be broken with very little exertion, and it seems that the physical structure and properties of such a deposit are very analogous to those of the brasses described in this paper, and that the very low tensile strengths are due to the same occluded impurities. Some runs in stationary baths show that a good brass may be deposited from a solution containing 130 grams potassium copper cyanide, 44 grams potassium zinc cyanide, and 65 grams of free potassium cyanide per liter. This corresponds to an approximate metal content of copper 53 and zinc 12 grams per liter. It is interesting to note the difference in the metal ratio in a bath which will give a good brass in a stationary solution, and that in a bath whose cathode is rotating at the rate of 4500 revolutions per minute. The free cyanide content is practically the same in both cases.

	Grams per liter	
	Stationary	Rotating
Copper	53.0	50.8
Zinc	11.5	7.1
Ratio: copper to zinc	1 : 0.22	1 : 0.14

This is accounted for by the fact that in the presence of free cyanide the electromotive force of copper is greater than that of zinc[1] and therefore zinc tends to deposit first. In the stationary cell, impoverishment of zinc at the cathode brings that metal content down to a value at which copper and zinc can be deposited simultaneously in the proportion required. The zinc content at the cathode is lower than that out in the body of the solution. With the rotating electrode, where impoverishment is prevented by rapid stirring, the concentration at the cathode is practically the same

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[1] Thompson: Proc. Roy. Soc., 42, 387 (1887).

as that throughout the whole solution. Consequently, the ratio of zinc to copper is necessarily lower than in the former case.

If this be true, there must be some limiting speed of the cathode above which brass will not deposit from a solution that will give it, in an unstirred bath. To test this, the solution just described for use in an unstirred bath was used, and a current density of 1 ampere per square decimeter maintained, while the speed of the cathode was varied.

The results are as follows:

Speed of cathode	Character of deposit
0	The usual stationary brass
500	No apparent change
1000	Still no apparent change
1500	The brass still is excellent
2000	Yellow brass depositing
2500	Deposit extremely high in zinc

Thus the speed 2000 gives to the solution sufficient agitation practically to nullify impoverishment of zinc for this particular current density, 1 ampere per square decimeter, and the purity of the zinc deposit becomes nearer and nearer to 100 percent as the speed of rotation is increased above that point.

In conclusion, therefore, it may be said that

1. Measurements have been made of the voltages required to deposit copper and zinc from a number of solutions, with rotating cathodes, the voltages being measured against an oxygen electrode.

2. Those solutions giving similar curves have been studied with a view to obtaining a good deposit of brass.

3. A brass was not obtained in any case, except from the cyanide solution.

4. The deposition of brass from cyanide solution is probably due to two factors: first, the tendency for the potentials of copper and zinc to become the same in the cyanide solu-

tion, and second, the increase in the potential of the more noble metal, by impoverishment.

5. The latter factor is practically eliminated by using the rapidly rotating cathode.

6. A *satisfactory* brass has not been deposited from the cyanide solution on the rotating cathode.

7. The brittleness of the alloy is probably due to occluded impurities. Hydrogen was removed from the alloy by heating in alkali.

8. The disturbing factor probably arises from the cyanide itself, which it seems impossible to eliminate.

9. The effect of impoverishment has been shown, by showing that a brass may be obtained up to a limiting speed of rotation of the cathode, beyond which zinc alone is deposited.

10. The metal ratio of copper to zinc in solutions for the deposition of a brass varies, not only with variations of free cyanide, but also with the rate of rotation of the cathode.

Electrochemical Laboratory
Cornell University

THE ELECTROMOTIVE BEHAVIOR OF SOLUBLE SULFIDES

BY ROGER C. WELLS[1]

One of the most characteristic properties of soluble sulfides, aside from their ability to form insoluble precipitates with many metals, is their reducing power. This is shown in the familiar reactions with ferric salts, chromates, ferricyanides, the halogens, nitro groups, nitric acid, and even sulfuric acid. If we consider this property to be essentially a property of sulfide ions the reduction of a ferric salt, for example, may be indicated by the equation

$$2Fe^{+++} + S^{--} = 2Fe^{++} + S$$

According to this equation the sulfide ions give up their negative charges while an equal number of positive charges are neutralized; free sulfur remains; no other ions appear to be directly concerned with the reducing action. The tendency of sulfide ions to give up their charges may also be shown by the production of an electric current when any unattackable conductor, such as platinum, is immersed in a soluble sulfide and properly connected to some other half cell such as the calomel electrode, yielding a cell combining two single potentials of this sort.

$$\mathrm{Hg} \mid \mathrm{HgCl} \mid N/1\ \mathrm{KCl} \mid \text{Soluble sulfide} \mid \mathrm{Pt}$$

The single potentials created by soluble sulfides under these circumstances may be designated sulfide potentials and the experiments to be described consisted in measurements of such potentials.

The single values were obtained by assigning the value 0.56 to the calomel electrode and neglecting diffusion potentials. Some of these values are shown in Table I, the positive sign indicating that the platinum was positive to the solution.

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[1] Published by permission of the Director of the United States Geological Survey.

TABLE I

Potentials of soluble sulfides

Solution in half cell	Sulfide potential
1 mole HCl per liter saturated with H_2S	+0.40
1 mole acetic acid saturated with H_2S	+0.29
KCl saturated with H_2S	+0.20
1 mole NaSH	—0.14
1 mole Na_2S	—0.27

Previous Work

In his measurements on oxidation cells Bancroft, in 1890, made a determination of the potential of a fifth molal solution of Na_2S, which by reference to a normal calomel electrode would yield the single potential —0.091.[1] This value does not fit in very well with my measurements. While studying the behavior of polysulfides Küster[2] obtained the value —0.239 for a normal solution of Na_2S with which my measurements agree to a few centivolts. Only a few other data, and these largely of an incidental character, have come to my attention.[3] In addition to the important contributions of Küster, however, there is one other suggestive paper by I. Bernfeld[4] in which it is shown that under certain conditions the sulfide potential observed can be calculated from the partial pressure of hydrogen sulfide in equilibrium with the solution used in the half-cell.

Chemistry of the Sulfide Electrode

It will be observed from Table I that when the sulfide electrode is coupled with the calomel electrode the potential of which is 0.56 volt, the current in every case tends to flow in a direction to make the platinum an anode, and hence to

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[1] Bancroft: Ueber Oxydationsketten, Zeit. phys. Chem., **10**, 387 (1892); cf. Neumann: Ueber das Potential des Wasserstoffs und einiger Metalle, Ibid., **14**, 228 (1894).

[2] Zeit. anorg. Chem., **44**, 445 (1905).

[3] Hittorf: Zeit. phys. Chem., **10**, 612 (1892). Two observations yielded —0.10 and —0.04 for 2.77 *N* KSH.

[4] Bernfeld: "Studien über Schwefelmetallelektroden," Zeit. phys. Chem., **25**, 46 (1897).

reduce mercurous ions to mercury. In other words the sulfide ions give up their negative changes, leaving free sulfur. This appears to be the primary action. When a feeble current (0.1 milliampere) was passed into a solution of hydrogen sulfide through a platinum anode a white cloud of sulfur was observed forming on the platinum and in the solution near the platinum; when sodium hydrosulfide or sodium sulfide was employed, however, sulfur was not a visible product nor was any gas evolved but after a time the solution turned yellow, indicating the formation of a polysulfide. The formation of a polysulfide may be considered a secondary effect due to the solution of sulfur freed by the current in the sodium hydroxide present, or it may be that polysulfide ions are an oxidation product of sulfide ions. Since polysulfides are not stable in acid solution we may postpone a consideration of them while we consider certain relations in acid solutions.

Let us consider the reversibility of the sulfide electrode. The spontaneous process sets sulfur free. The reverse process therefore appears to demand that sulfur should ionize. Several experiments were made to see if free sulfur under any circumstances in contact with platinum could be made to ionize. A platinum electrode coated with sulfur was allowed to stand in normal potassium chloride in a closed half-cell for a long period. The effect was in the direction expected but it would have required several weeks to reach a correct sulfide potential in that way, if it ever could be reached. A similar electrode in caustic soda gave low values in the course of two days but as it is well known that sulfur dissolves in alkali hydroxides at an appreciable speed the production of a low potential in this way may be regarded wholly as a "chemical" action and the electromotive effect secondary. The experiments were therefore inconclusive as to whether the platinum assisted the ionization of the sulfur at all.

Effect of Hydrogen

On the other hand, if a current is passed in a direction to make the platinum a cathode hydrogen is probably set free under ordinary circumstances. Even if it is not visibly evolved it is probably dissolved somewhat by the platinum or it may combine with sulfur to form hydrogen sulfide. No difficulty was ever experienced, using a Lippman electrometer, in approaching the point of balance from either direction although I preferred to approach it from the side to set sulfur free. The object of this procedure was to have the solution saturated with sulfur.

TABLE II

Effect of hydrogen in platinized electrodes used in sulphide solutions

Electrode	Time	Cell Hg+	Platinum	Remarks
A freshly platinized electrode, soaked an hour in hot water	1.23	0.12	+0.44	
then touching $N/1$ NaOH in bottle	1.32	0.13	+0.43	An oxygen value
H_2 turned on	1.37	1.06	—0.50	Correct hydrogen value
	1.40	1.07	—0.51	
	3.07	1.07	—0.51	
Electrode now touched to colorless $N/1$ Na_2S	4.00	0.96	—0.40	
	4.02	0.90	—0.36	A variable intermediate value
	4.07	0.88	—0.32	
	5.00	0.86	—0.30	
	next day, 9.00	0.88	—0.32	
Smooth electrode	10.00	0.80	—0.24	Correct sulfide potential
	10.30	0.79	—0.23	
	11.00	0.80	—0.24	

Ordinary hydrogen sulfide made from commercial ferrous sulfide contains considerable hydrogen. A number of experiments were therefore made to find out if hydrogen could cause an error in the determination of sulfide potentials. It was found that hydrogen might easily cause an error in acid solutions where the concentration of sulfide ion is small but that it was of doubtful influence in alkaline solutions containing a high concentration of sulfide. In fact it seemed of assistance in the alkaline solutions in preventing oxidation. It is generally assumed that smooth electrodes are best for measuring most oxidation potentials but that platinized electrodes are desirable for hydrogen, iodine, bromine and chlorine electrodes. I was therefore somewhat surprised to find that hydrogen showed its effect rather quickly even with smooth electrodes in acid solution, whereas in the alkaline sulfide solutions I found it impossible to obtain correct hydrogen potentials even with well-platinized electrodes. The variability of a platinized electrode in sodium sulfide is shown in Table II.

When an error from hydrogen was feared pure hydrogen sulfide was employed instead, prepared from alkali sulfide and hydrochloric acid and washed with sodium hydrosulfide.

Relation between Concentration and Potential

In seeking for a mathematical elucidation of sulfide potentials we may assume the process at the electrode, at least in one direction, to be

$$S^{--} = S + 2\theta \qquad (1)$$

which would yield as the most general expression possible for the potential

$$E = E_0 - \frac{0.059}{2} \log \frac{[S^{--}]}{[S]} \qquad (2)$$

in which the bracketed symbols stand for concentrations.

We are uncertain about the number of atoms in a molecule of sulfur but it is obvious that the proper equation would yield the same value of E_0 whatever the complexity of the sulfur molecule. Further, we know that the concentration of free sulfur soluble in water is exceedingly small, so small that a very small current must suffice to liberate enough to form a saturated solution. If we take the concentration of free sulfur in a saturated solution to be constant and part of E_0 the only remaining variable is the concentration of sulfide ions. Let us calculate values of E_0 therefore from sulfide ion concentrations so far as they are known.

Fortunately the sulfide ion concentrations of the salts concerned have already been deduced by Knox.[1] The essential equation is

$$[S^{--}] = \frac{1.1 \times 10^{-23}}{[H^+]^2} \qquad (3)$$

an expression giving the sulfide ion concentration for any solution whose hydrogen ion concentration is known. Table III gives the sulfide ion molality of the solutions investigated, the potential observed, the value of E_o calculated by equation (2) taking the concentration of free sulfur as unity and also the value of E calculated from the mean value of E_o.

TABLE III

Solution	Sulphide ion concentration	E_o calculated	E observed	E calc. from E_o
1 mole HCl + H_2S	1.1×10^{-23}	—0.27	+0.40	+0.41
1 mole acetic acid + H_2S	0.6×10^{-18}	—0.24	+0.29	+0.27
1 mole KCl + H_2S	1.2×10^{-15}	—0.23	+0.20	+0.17
1 mole NaSH	3.6×10^{-5}	—0.27	—0.14	—0.13
1 mole Na_2S	0.09	—0.30	—0.27	—0.23
	mean	—0.26		

There is fair approach to constancy in the values of E_o. Equation (2) is therefore significant in view of the enormous range of the sulfide ion concentration and appears to be applicable to the determination of sulfide ion concentrations under some conditions. Of the values in Table III, those for NaSH and Na_2S are the least certain and the behavior of these two salts must therefore be considered further.

Preparation of Sodium Hydrosulfide

Küster and Heberlein[2] recommend metallic sodium as the best substance with which to start if for any reason sodium hydroxide will not suffice. If it is desired to avoid all oxidized products it is advisable to pass a current of hydrogen through

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[1] J. Knox: "A Study of the Sulfur Anion and of Complex Sulfur Anions." Trans. Faraday Soc., 4, 47 (1908).

[2] Küster and Heberlein: Zeit. anorg. Chem., 3, 55 (1905).

the sodium hydroxide before introducing hydrogen sulfide, at the same time having a piece of platinum in the bottle to make the hydrogen more effective through electrolytic action. The saturation of sodium hydroxide with H_2S yields a solution containing a considerable excess of H_2S. Part of this excess may be removed from a solution as concentrated as normal by bubbling a stream of hydrogen through it for some hours. Since both Na_2S and NaSH yield an alkaline reaction the neutral point is passed while there is still a slight excess of H_2S. The changes in the solution from the first introduction of H_2S to saturation and expulsion of excess may be followed with advantage by potential measurements. The results of one experiment in which the excess of H_2S in normal NaSH was neutralized by adding NaOH from a burette are shown in Fig. 1.

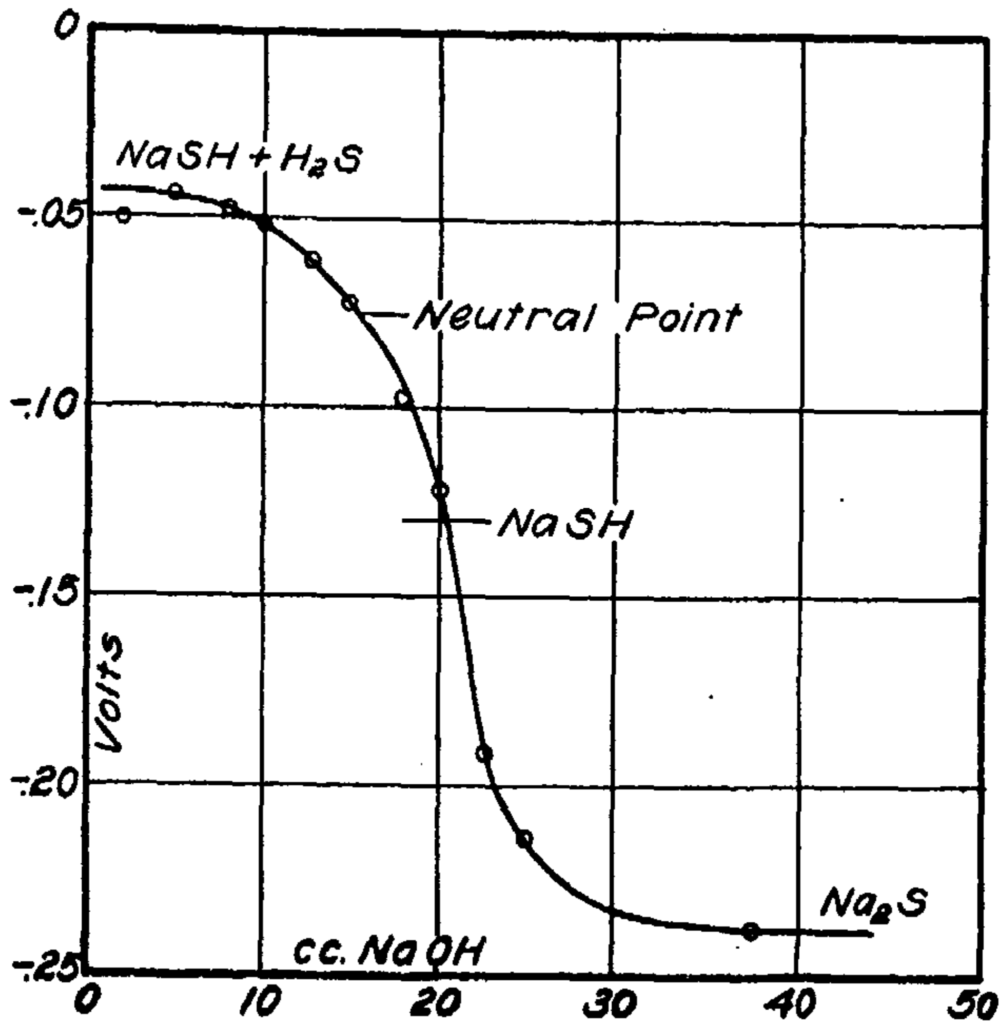

Fig. 1

It is evidently impossible to decide from the figure just what is the proper potential for NaSH. The value —0.14

was chosen before the relations described above were worked out, but was omitted in deriving the average for E_0. The potential calculated for NaSH by equation (2) is —0.13.

Behavior of Sodium Sulfide

It is rather difficult to obtain potentials corresponding to pure Na_2S solutions. Equation (2) suggests that this variability may be due to an uncertain concentration of free sulfur. In action an electrode bathed by Na_2S may generate polysulfide and there is not the same limitation set by the saturation with sulfur as appears to obtain in acid solutions. Moreover, it has been found that polysulfides are reduced by the reverse current instead of hydrogen being set free. Solutions containing polysulfides therefore give very definite potentials and their behavior is somewhat like that of ferro-ferricyanide mixtures. It was found, however, that the potential varies considerably with the dilution, depending on the amount of polysulfide present. These results are shown graphically in Fig. 2.

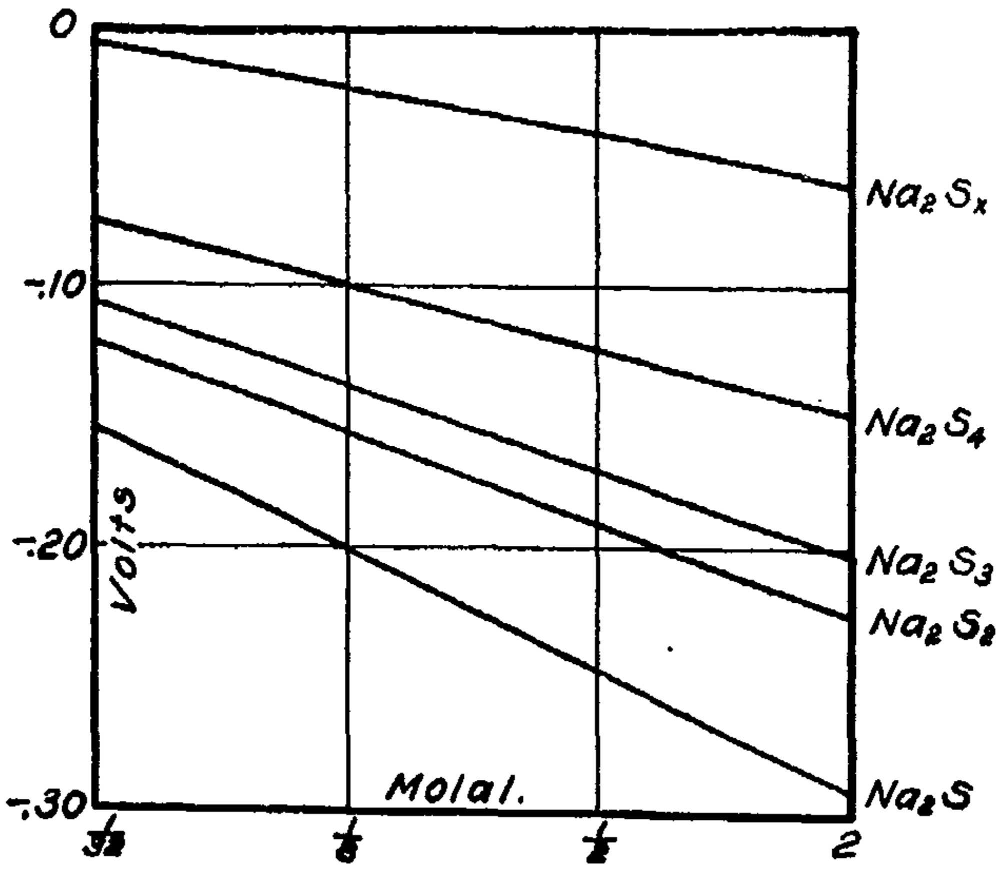

Fig 2

A little calculation shows that the behavior of the saturated polysulfides, Na_2S_x, on dilution is more in harmony with equation (2) than that of the other solutions. Many attempts were made to express the behavior of the other solutions by an equation involving only two molecular species. like ferro-ferricyanide mixtures, but without complete success. Doubtless there are more than two molecular species possible. It appears, however, that there is some basis for neglecting the species Na_2S_2 and Na_2S_3, and considering such solutions to be chiefly mixtures of Na_2S and Na_2S_4. The grounds for this will be somewhat evident from a consideration of Fig. 3 in which are shown the changes in potential as the composition of the solution is varied from Na_2S to Na_2S_x.

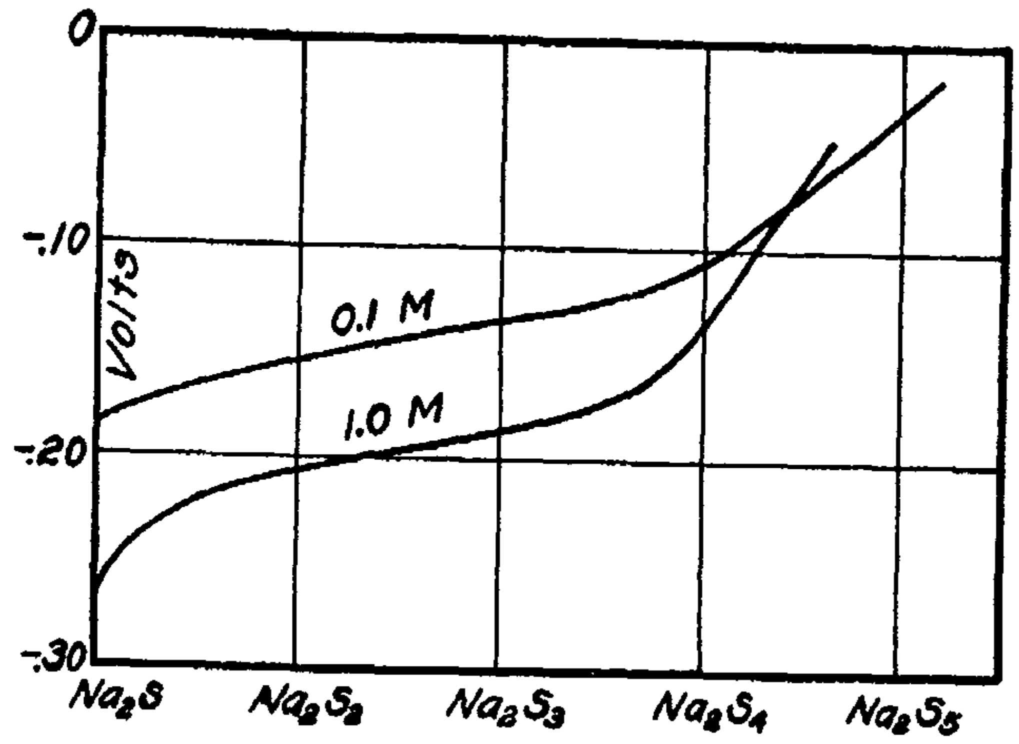

Fig. 3

Starting with pure Na_2S we may assume that the first oxidation product is disulfide according to the reaction

$$2S^{--} = (S_2)^{--} + 2\theta \tag{4}$$

We should then have a relation for the oxidation-reduction potential like

$$E = E_0 - \frac{0.059}{2} \log \frac{[S^{--}]^2}{[(S_2)^{--}]} \tag{5}$$

A test of this equation was made by resolving solutions of compositions between Na_2S and Na_2S_2 into the proper mixtures of the two species and assuming the ionic concentrations to be proportional to the molal. Suffice it to say that the equation did not yield a constant value of E_0. In fact the shape of the potential curve suggests that the second species must be more complex than Na_2S_2. Apparently an excess of sulfur forms at once a higher polysulfide than Na_2S_2. The nearest approach to a uniform slope in the curve falls between Na_2S_2 and Na_2S_3 indicating that if Na_2S is one member the other is nearly as complex as Na_2S_4. The electrical oxidation would then be

$$4S^{--} = (S_4)^{--} + 6\theta \qquad (6)$$

giving for the potential the expression

$$E = E_0 - \frac{0.059}{6} \log \frac{[S^{--}]^4}{[(S_4)^{--}]} \qquad (7)$$

An evaluation of E_0 by this equation is shown in Table IV.

TABLE IV

Composition, x in Na_2S_x	Formal concentrations of		Potential observed	E_0 calculated by (7)
	Na_2S	Na_2S_4		
1.50	0.83	0.17	—0.220	—0.215
1.75	0.75	0.25	—0.212	—0.211
2.00	0.67	0.33	—0.206	—0.208
2.25	0.58	0.42	—0.201	—0.207
2.50	0.50	0.50	—0.197	—0.206
2.75	0.42	0.58	—0.192	—0.205
3.00	0.33	0.67	—0.188	—0.205
3.25	0.25	0.75	—0.183	—0.205
3.50	0.17	0.83	—0.175	—0.204

It will be seen on referring to the table that equation (7) gives a fairly constant value of E_0 from Na_2S_2 to Na_2S_3. No equation as complicated as this has to my knowledge been applied to potential measurements before, although Fredenhagen suggested such equations.[1] An equation corresponding to the intermediate possibility, namely,

$$3S^{--} = (S_3)^{--} + 4\theta$$

was found less satisfactory than equation (7).

The conclusions from the preceding discussion are then as follows: The electromotive behavior of the polysulfides resembles that of other oxidation-reduction potentials in a general way. Although it is impossible to account for the behavior without assuming that several species are present in a rather complicated equilibrium it appears unnecessary to consider Na_2S_2 one of them or possibly even Na_2S_3. The potentials may be calculated as if they depended on the relative concentrations of the two species Na_2S and Na_2S_4 for the range from Na_2S_2 to Na_2S_3. On reaching a composition near Na_2S_4 a rapid shift to a much higher sulfide is suggested. The excess sulfur is of course presumed to form complex anions.

On the other hand, in solutions which are easily saturated with sulfur the simple equation

$$E = -0.26 - 0.029 \log [S^{--}]$$

appears to express the electromotive behavior of soluble sulfides very well.

Washington, D. C.
April, 1914

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[1] C. Fredenhagen: "Zur Theorie der Oxydations- und Reductions-ketten." Zeit. anorg. Chem., 29, 444 (1902).

THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN PEROXIDE. II

J. HOWARD MATHEWS AND HARRY A. CURTIS

Introduction

The decomposition of hydrogen peroxide by light is a reaction which is extraordinarily sensitive to the influence of catalysts, both positive and negative. Our first paper on the photolysis of hydrogen peroxide[1] discussed the inhibition of the photo-reaction by sulphuric acid, sodium chloride, acetanilide, calcium hydroxide, sodium hydroxide and barium hydroxide. It was pointed out that the same catalysts act differently toward the thermal and the light decomposition of hydrogen peroxide. For example, sodium hydroxide, which greatly increases the rate of decomposition at 80°, acts as a preservative in the photo-reaction; calcium hydroxide, which has no effect on the thermal decomposition, inhibits the photolysis. On the other hand, sulphuric acid and acetanilide inhibit both the thermal and the photo-decompositions.

We have extended the investigation of the catalysis of the photo-reaction to a number of other catalysts with the results indicated below.

Experimental Methods and Data

The apparatus used to study the catalysis of the photo-reaction was the same as described in our first paper,[1] and we also used the same methods of preparing the peroxide solution and of following the course of the reaction.

In the graphs shown below, curves marked I represent, in every case, the course of the reaction before adding the catalyst, and curves marked II, the course of the reaction after adding the catalyst. The sudden break between curves I and II represents the dilution effect of adding the catalyst, as we have previously shown.

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[1] Jour. Phys. Chem., 18, 166 (1914).

Effect of Urea

Urea is without appreciable effect on the reaction. Table I and Fig. 1 show the course of the reaction. The amount of urea added was such as to make the whole solution 0.05 percent.

Table I

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	7.03	141	6.38
33	6.90	167	6.29
62	6.81	193	6.20
93	6.68	215	6.11
121	6.57	235	6.05
Added urea at 134			

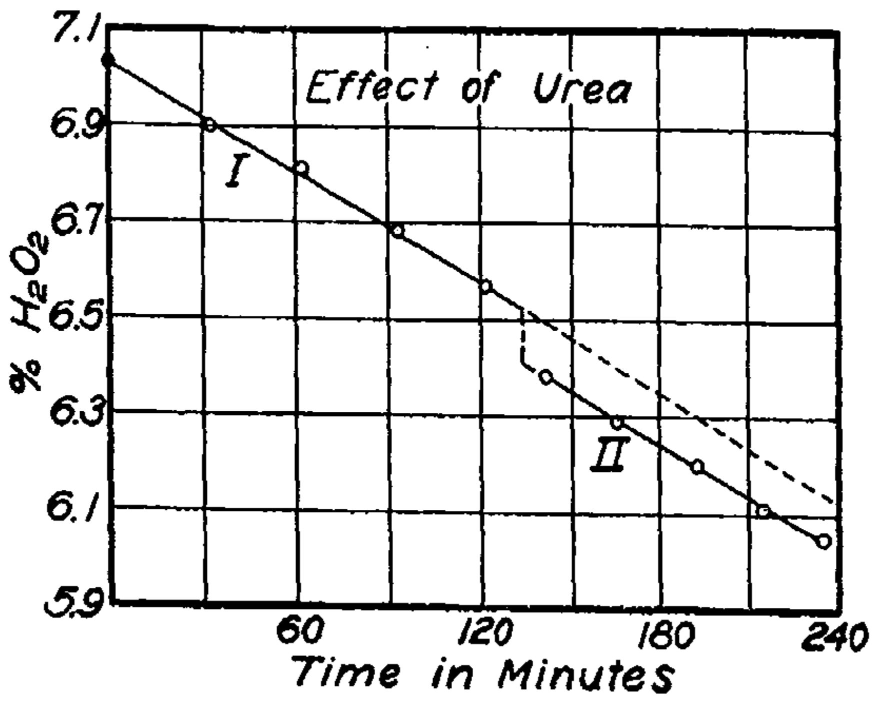

Fig. 1

Effect of Acetic Acid

Acetic acid acts as a mild preservative. Table II and Fig. 2 refer to acetic acid.

TABLE II

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	7.04	117	6.47
41	6.88	142	6.44
70	6.77	169	6.39
102	6.63	203	6.30
Added acetic acid at 110		250	6.24

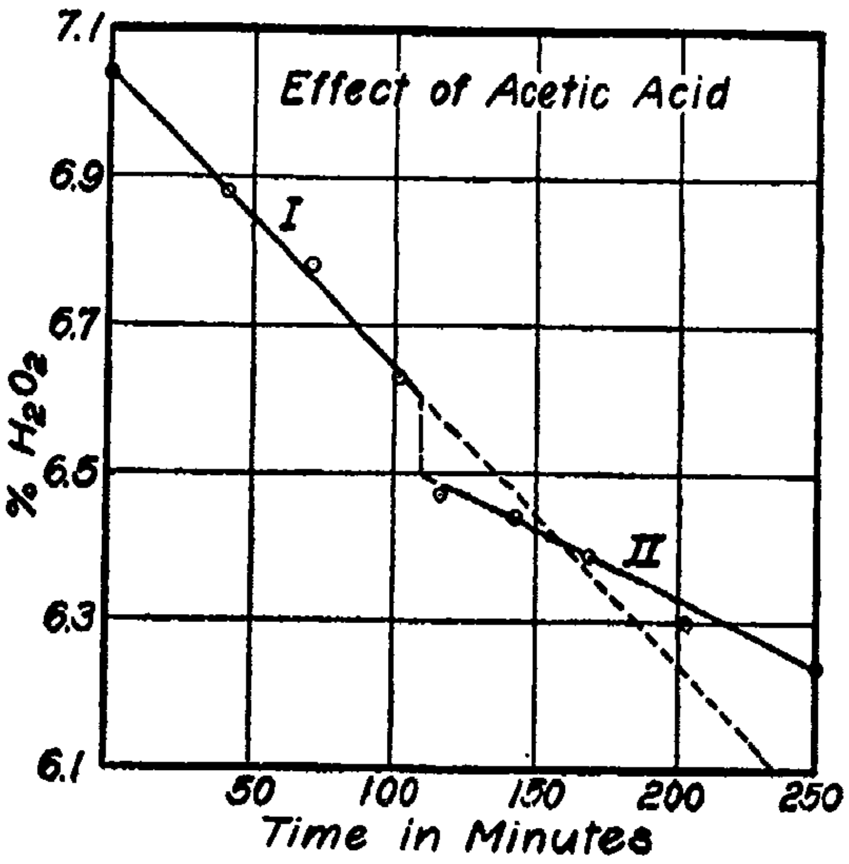

Fig. 2

Effect of Boric Acid

Boric acid has no effect on the reaction, as Table III and Fig. 3 show. The amount of boric acid added was such as to make the whole solution 0.044 percent.

TABLE III

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	4.61	120	4.24
38	4.51	146	4.16
71	4.43	187	4.06
97	4.36	221	3.97
Added the boric acid at 106			

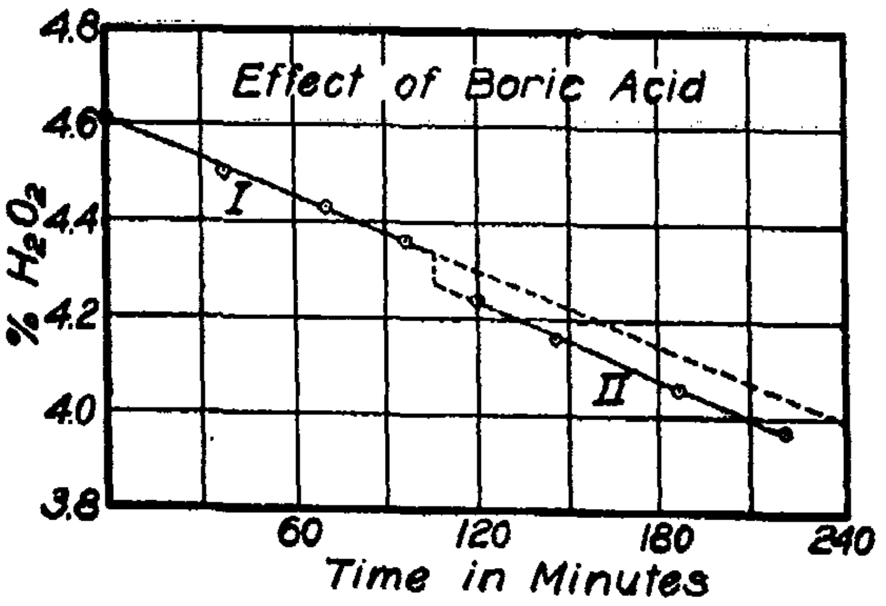

Fig. 3

Effect of Tartaric Acid

Tartaric acid is a mild preservative. In this experiment the acid was added in the solid form, and the dilution effect is therefore absent in Fig. 4. The amount of acid added was such as to make the whole solution 0.096 percent.

Table IV

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	4.53	120	4.26
38	4.43	163	4.225
76	4.35	199	4.20
106	4.27		
Added tartaric acid at 112			

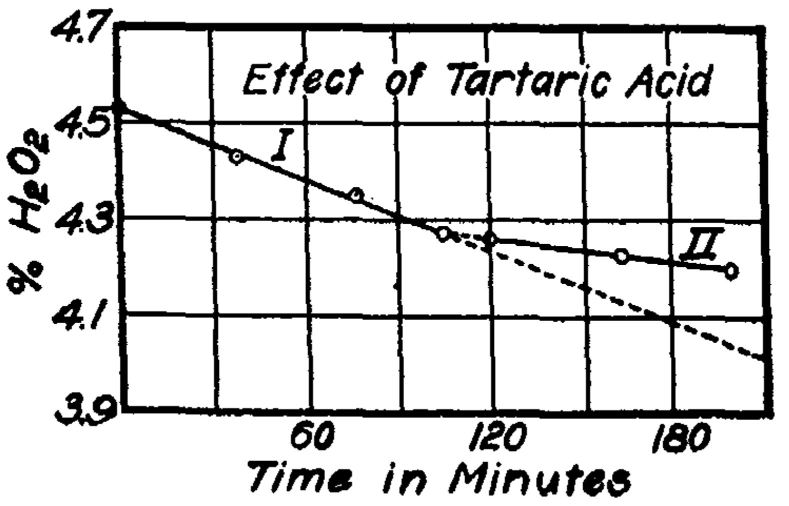

Fig. 4

Effect of Phosphoric Acid

The effect of phosphoric acid is similar to that of acetic acid and of tartaric acid, inhibiting the reaction. The amount of acid added was such as to make the whole solution 0.152 percent.

TABLE V

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	4.425	80	4.21
29	4.34	110	4.16
59	4.26	139	4.13
Added phosphoric acid at		171	4.10
69			

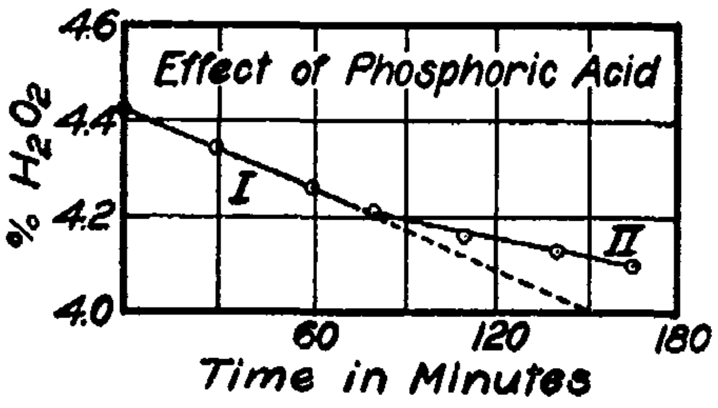

Fig. 5

Effect of Benzoic Acid

This acid is an excellent preservative. Table VI and Fig. 6 show the effect of benzoic acid on the photolysis.

TABLE VI

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	3.32	156	3.04
29	3.27	187	3.01
69	3.20	217	3.02
109	3.14	247	3.01
131	3.09		
Added benzoic acid at			
146			

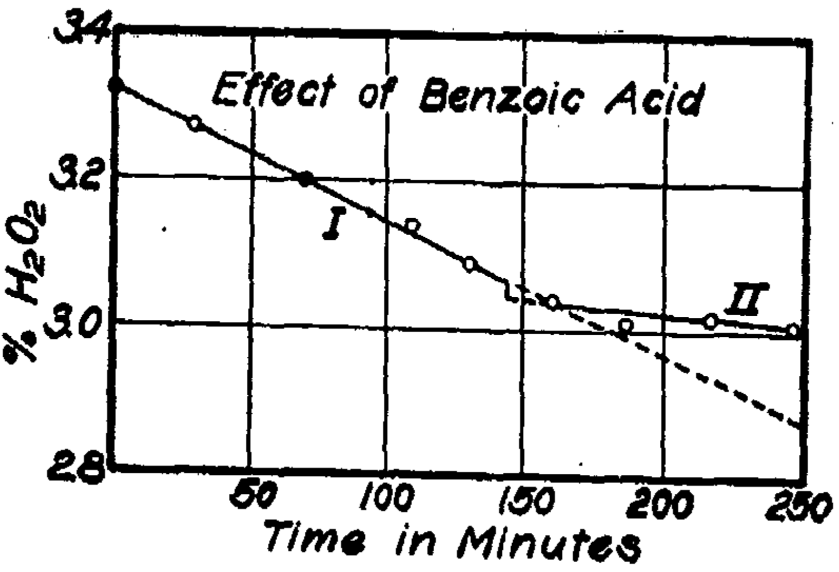

Fig. 6

Effect of Barium Chloride

The addition of this salt has no effect on the rate of the photolysis, as Table VII and Fig. 7 show. The amount of barium chloride added was such as to make the whole solution 0.037 percent.

TABLE VII

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	3.85	108	3.61
43	3.78	156	3.52
88	3.70	196	3.45
Added $BaCl_2$ at 102			

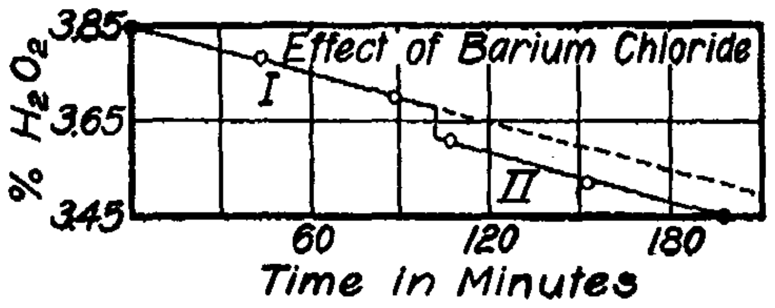

Fig. 7

Effect of Barium Nitrate

Barium nitrate increases the rate of decomposition. This is a striking fact in view of the strong preserving action of barium hydroxide and the zero effect of barium chloride. Table VIII and Fig. 8 present the results for barium nitrate. The amount of salt added was such as to make the whole solution 0.037 percent.

Table VIII

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	3.77	109	3.49
41	3.69	147	3.38
80	3.62	190	3.26
Added $Ba(NO_3)_2$ at 91			

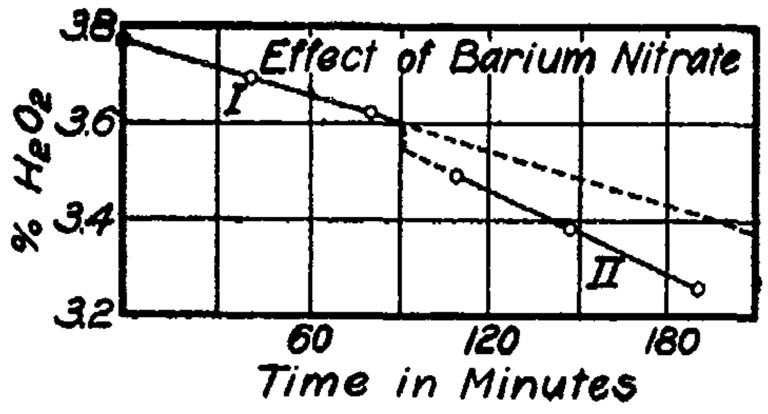

Fig. 8

Effect of Potassium Chloride

Potassium chloride, like sodium chloride, very slightly decreases the rate of photolysis. It will be seen in Table IX and Fig. 9 that for some time after the catalyst was added the rate of decomposition remained unchanged and then began to fall off very slowly. The amount of the salt added was such as to make the whole solution 0.023 percent.

Table IX

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	3.68	119	3.40
38	3.60	154	3.32
78	3.52	189	3.24
Added KCl at		227	3.18
92		245	3.15

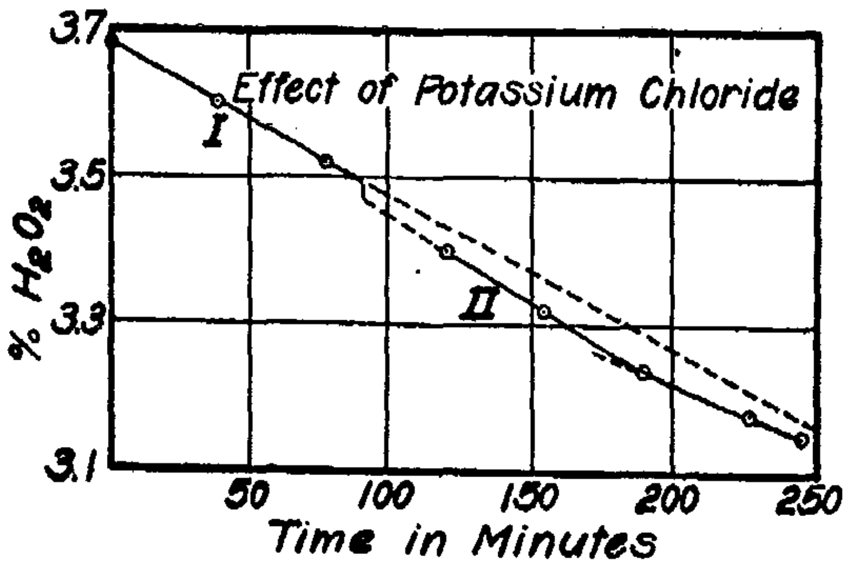

Fig. 9

Effect of Sodium Chloride

We have previously shown that sodium chloride slightly decreases the rate of photolysis of peroxide. After noting the lag in the inhibiting effect of potassium chloride, we repeated the experiment with sodium chloride, using a 0.011 percent solution instead of the 0.05 percent solution used before, and also cutting down the light intensity to that used in the potassium chloride experiment. Under these conditions we found the same lag in the inhibiting effect of sodium chloride. Table X and Fig. 10 present the results of this experiment.

Table X

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	3.57	94	3.27
39	3.47	130	3.17
74	3.375	159	3.13
Added NaCl at		189	3.07
83		218	3.02

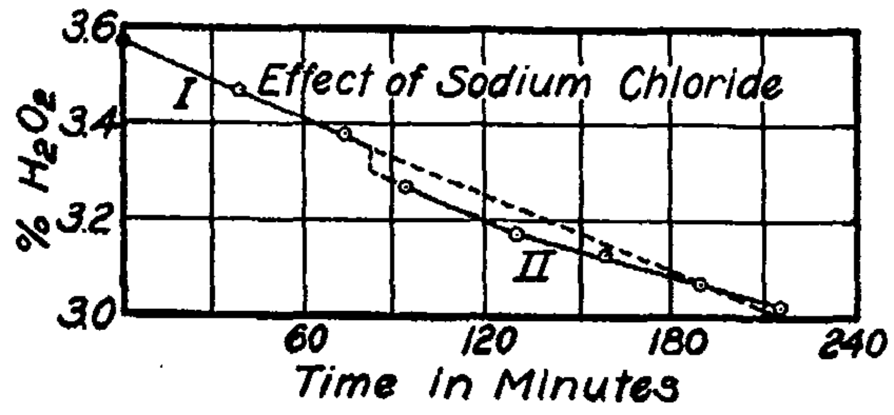

Fig. 10

Effect of Acetamide

As acetanilide has such a strong inhibiting action, acetamide naturally suggested itself as another possible catalyst. This substance has, however, practically no effect on the rate of photolysis, as Table XI and Fig. 11 show. The amount of acetamide added was such as to make the whole solution 0.037 percent.

TABLE XI

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	3.39	104	3.09
35	3.31	139	3.00
72	3.22	172	2.94
Added acetamide at 80		206	2.86

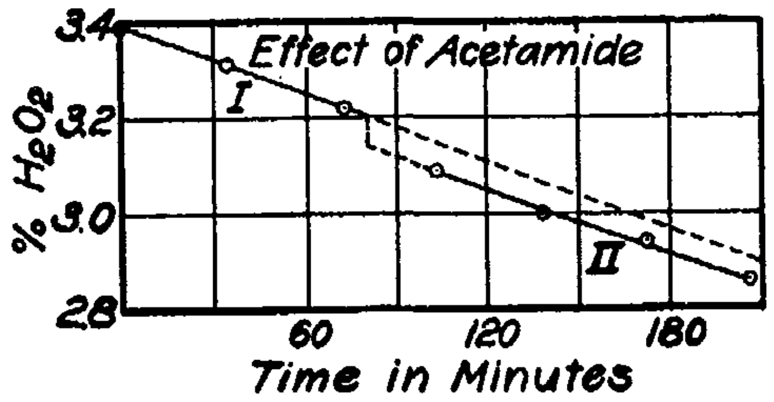

Fig. 11

Effect of Potassium Nitrate

Potassium nitrate has at first no effect on the reaction, but after it has been present for some time begins to inhibit the photolysis slightly, resembling in this behavior the action of sodium and potassium chlorides. In Table XII and Fig. 12 are given the results for potassium nitrate. The amount of nitrate added was such as to make the whole solution 0.031 percent.

Table XII

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	3.34	114	3.00
31	3.25	149	2.91
65	3.18	184	2.87
98	3.09	197	2.85
Added KNO_3 at 105		227	2.81

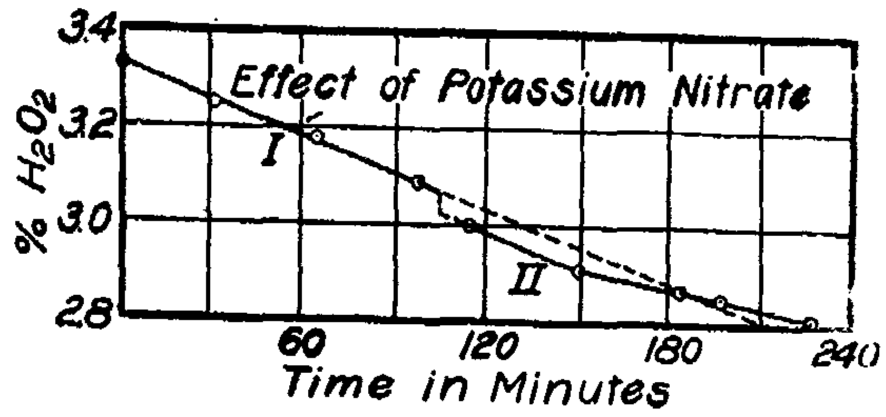

Fig. 12

Relation between the Amount of the Catalyst Added and the Magnitude of Effect Produced

The effect produced by a catalyst on the photolysis of hydrogen peroxide is not directly proportional to the amount of the catalysts used. We have tried sulphuric acid of four concentrations approximating very closely the ratios 1 : 10 : 100 : 200.[1] Table XIII and Fig. 13 show the effect of sulphuric acid 0.000175 *N*; Table XIV and Fig. 14 of sulphuric acid 0.00176 *N*; Table XV and Fig. 15 of sulphuric

Table XIII

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	4.90	117	4.52
35	4.81	143	4.50
62	4.74	171	4.45
89	4.68	205	4.39
Acid added at 98 Conc. 0.000175 *N*		229	4.34

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[1] The concentrations of the acid used were exactly of these ratios, but the volume of the peroxide solution at the time of adding the acid was not the same in each case.

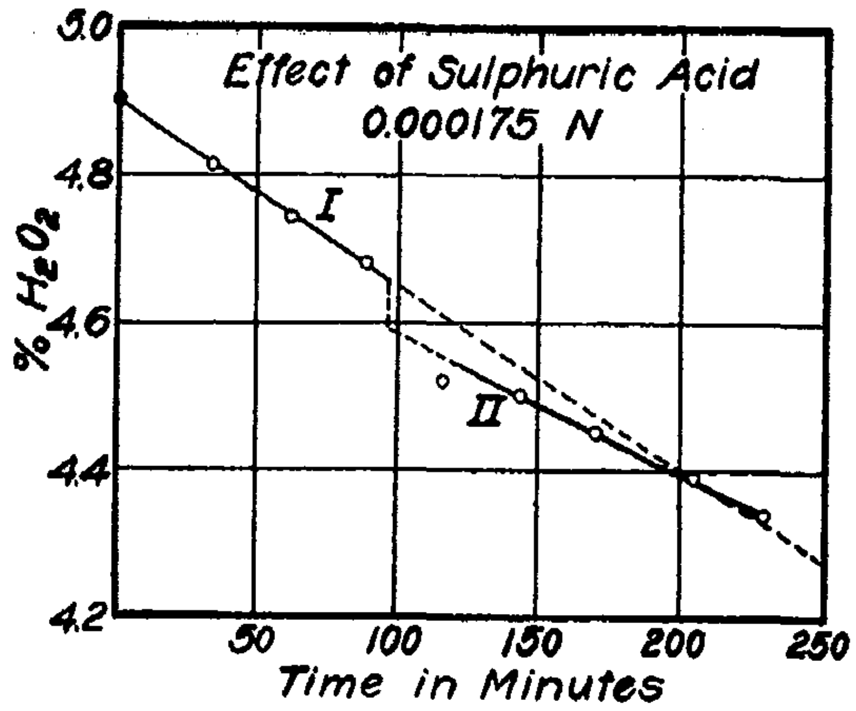

Fig. 13

acid 0.0176 N; and Table XVI and Fig. 16 of sulphuric acid 0.0349 N.

TABLE XIV

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	5.21	85	4.90
22	5.13	106	4.86
42	5.07	130	4.86
63	5.00	153	4.83
Acid added at		176	4.80
72		199	4.78
Conc. 0.00176 N		224	4.77

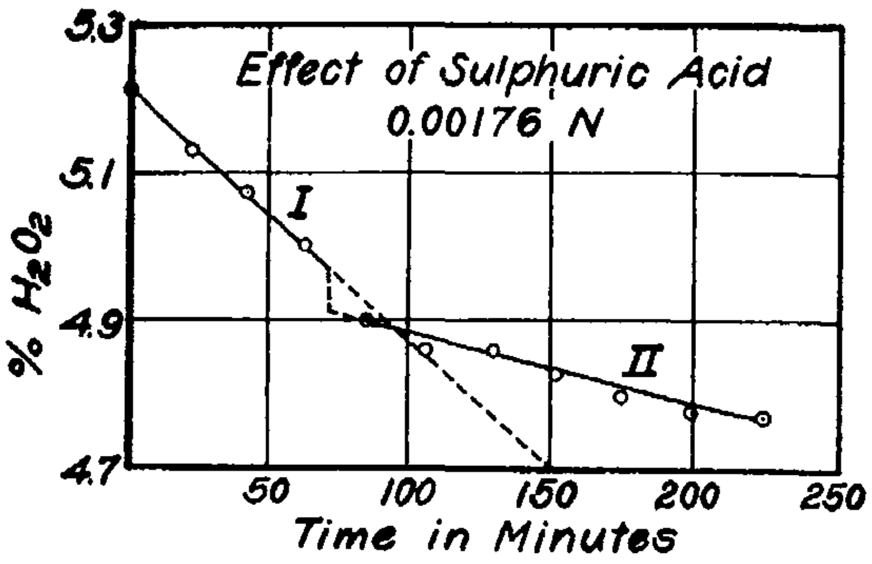

Fig. 14

TABLE XV

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	5.31	176	4.81
28	5.23	197	4.80
55	5.13	226	4.78
85	5.06	255	4.76
124	4.94		
Added acid at			
132			
Conc. 0.0176 *N*			

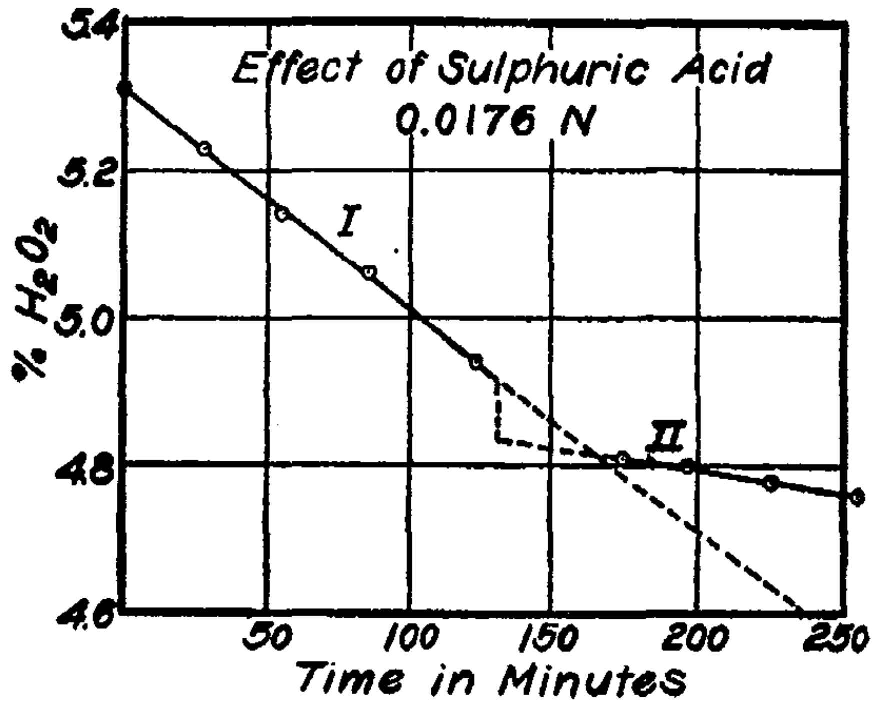

Fig. 15

TABLE XVI

Time in minutes	Percent H_2O_2	Time in minutes	Percent H_2O_2
0	5.19	152	4.74
36	5.10	181	4.725
71	4.99	222	4.69
119	4.88	257	4.68
Added acid at			
128			
Conc. 0.0349 *N*			

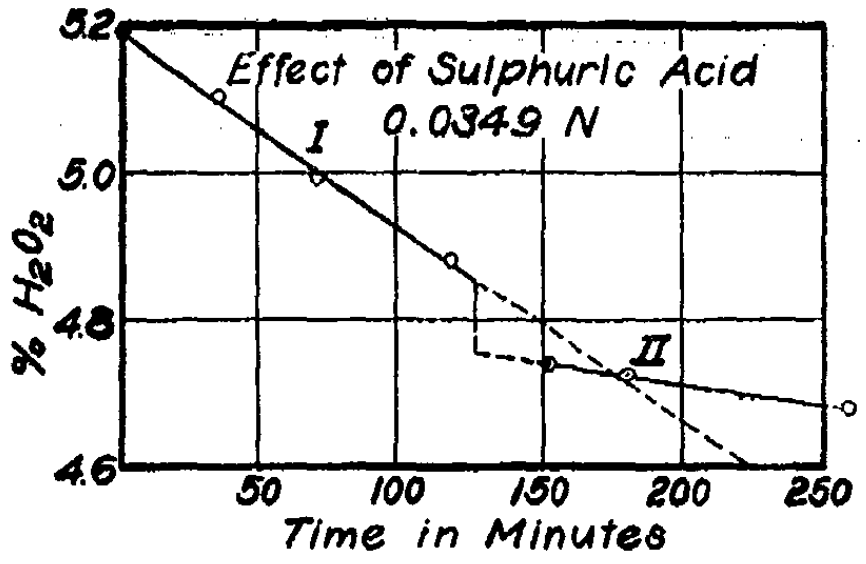

Fig. 16

The ratio of the slope of Curve II to that of Curve I will, in each case, give us a measure of the effect of the acid, since for concentrations of peroxide such as used in these experiments the rate of the decomposition is practically linear.

These ratios are as follows: for 0.000175 *N* acid, 0.76, *i. e.*, the rate after adding the acid was about 76 percent of the rate before adding the acid; for 0.00176 *N* acid, 0.30; for 0.0176 *N* acid, 0.20; for 0.0349 *N* acid, 0.22.

It will be seen that the two higher concentrations of acid have practically the same effect; the effect is a little less for the 0.0176 *N* acid, and very much less for the most dilute of the four. Judging from these results, which are, perhaps, not extensive enough to be conclusive, it appears that while the magnitude of the catalytic effect varies in the same direction as the concentration, the two are by no means directly proportional. And further, that above a certain concentration, the catalytic effect becomes nearly constant.

We have noted the same behavior in the case of the catalysis by means of sodium chloride. After changing the rate of the photolysis by adding 0.006 gram of salt, the further addition of 0.5 gram had no effect on the rate of decomposition.

The Absorption of Light by Hydrogen Peroxide Solutions

We have attempted to find a relationship between the change of light absorption in the peroxide solution upon adding the catalyst and the effect produced. The change is too small to be measured with any certainty by the Rubens' linear thermopile. The photographic method used by Henri[1] was also tried. The results showed qualitatively that the absorption is very slightly increased by adding the catalyst, but threw no light upon the specific nature of catalytic effect.

Henri and Wurmser have noted[2] that the addition of an alkali to a peroxide solution increases its absorption in the ultraviolet, but found no connection between the absorption and the nature of the catalyst. It might be expected that such an increase in absorption would increase the rate of decomposition, rather than decrease it as is actually the case.

The Surface Tension of Hydrogen Peroxide Solutions

W. Spring[3] has shown that the surface tension of pure hydrogen peroxide is only about 45 percent that of pure water at 10°, and that it increases very rapidly as water is added. Our own measurements indicate that the surface tension of a 5 percent solution of peroxide is slightly less than that of pure water. The change in surface tension of a hydrogen peroxide solution on adding a small amount of acid or of alkali is exceedingly small. We at first attempted to detect a difference using a stalagmometer. While this instrument would show the difference between the surface tension of pure water and peroxide solution it would not detect any change when a small amount of acid was added to the peroxide.[4]

On applying the capillary tube method, and reading the heights of the column in the capillary with an excellent cathetometer, we found that a trace of sulphuric acid would lower the surface tension slightly. A trace of alkali had but little effect, while a larger amount would very slightly increase the surface tension.

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[1] Phys. Zeit., 14, 515 (1913).

[2] Comptes rendus, 157, 284 (1913).

[3] Zeit. anorg. Chem., 8, 424 (1895).

[4] The stalagmometers at hand have a capacity of only about 42 drops for water, and the accuracy on small changes of surface tension would naturally not be great.

W. Spring[1] compared the surface tension of an acid solution of peroxide with that of an alkaline solution of the same density, finding the surface tension of the alkaline solution to be a few percent higher than that of the acid solution.

Since both sulphuric acid and sodium hydroxide decrease the rate of photolysis of hydrogen peroxide, it does not seem that an explanation of catalytic effect is to be found in the slight changes of surface tension. Moreover, the change in the rate of photolysis of hydrogen peroxide on adding a trace of a catalyst is altogether out of proportion to the change in surface tension of the solution as a result of adding a catalyst.

The Chemical Nature of the Catalysts and their Specific Catalytic Effect

We tabulate below the various catalysts we have tried (including those for which the data were given in our previous paper) and their influence on the rate of photolysis of hydrogen peroxide.

TABLE XVII

Substance	Amount used Percent	Effect on photolysis
Acetanilide	0.04	Strong inhibition
Acetamide	0.037	Practically no effect
Urea	0.05	Practically no effect
Acetic acid		Mild inhibition
Benzoic acid		Strong inhibition
Boric acid	0.044	No effect
Tartaric acid	0.096	Mild inhibition
Phosphoric acid	0.152	Mild inhibition
Sulphuric acid	0.000875	Slight inhibition
Sulphuric acid	0.008624	Mild inhibition
Sulphuric acid	0.08624	Mild inhibition
Sulphuric acid	0.17101	Mild inhibition
Calcium hydroxide	0.002	Strong inhibition
Sodium hydroxide	0.053	Strong inhibition
Barium hydroxide	0.007	Strong inhibition
Barium chloride	0.037	No effect
Barium nitrate	0.037	Increases rate
Potassium nitrate	0.031	Very small inhibition
Potassium chloride	0.023	Very small inhibition
Sodium chloride	0.011	Very small inhibition
Sodium chloride	0.05	Mild inhibition

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[1] Zeit. anorg. Chem., 10, 161 (1895).

The table clearly emphasizes the specific catalytic action of the substances used. Aside from this, there are but few regularities to be found in the table. It will be noted that all the alkalies tried inhibit the reaction; of the acids, benzoic is an excellent preservative, sulphuric, acetic, tartaric, phosphoric are mild preservatives, while boric acid is without effect; of the neutral salts, barium nitrate hastens the photolysis, barium chloride is without effect, while potassium chloride, sodium chloride and potassium nitrate have a very small inhibiting effect after they have been present in the solution for some time. Acetanilide is an excellent preservative, while urea and acetamide are without effect.

The influence of foreign substances on the *thermal* decomposition of hydrogen peroxide has been the subject of a considerable amount of investigation and a great deal of speculation. The reason for the effects has not yet been discovered. The problem is, of course, a special case of the broader phenomenon of catalysis in general, which phenomenon yet remains to be explained by any theory to which experimental data can be applied.

When more is known about catalysis in general, it may be possible to explain why sulphuric acid strongly inhibits the thermal decomposition of hydrogen peroxide, while sodium hydroxide is a strong positive catalyst for the thermal reaction. It will then remain to show why both of these substances inhibit the photolysis of hydrogen peroxide.

Summary

1. The influence of a number of inorganic and organic compounds on the rate of photolysis of hydrogen peroxide has been measured quantitatively.

2. The same catalysts do not effect the thermal decomposition and the photochemical decomposition of hydrogen peroxide in the same way.

3. There is no general relationship between the chemical nature of a compound and its catalytic effect on the photolysis of hydrogen peroxide.

4. While the magnitude of the catalytic effect and the concentration of the catalyst vary in the same direction, there is not a direct proportionality between these two quantities.

5. Neither the change in the light absorption nor the change in surface tension of a hydrogen peroxide solution brought about by the addition of a small amount of a catalyst seems adequate to explain the marked catalytic effect produced.

Laboratory of Physical Chemistry
University of Wisconsin
April, 1914

NEW BOOKS

Chemistry and Its Borderland. *By Alfred W. Stewart. 14 × 20 cm; vii + 314. Longmans, Green & Co., 1914. Price: $1.50 net.*—In the preface the author says: "At the present time the sciences and their applications are playing a preponderant part in our daily existence; and yet, so involved are their ramifications that very few people realize the closeness of contact between science and modern life. An interest in the progress of scientific investigation is becoming more marked, however, and a demand is springing up for information upon recent advances in the scientific field.

"This demand is easy to supply in certain branches of science; for some lines of scientific thought lend themselves more easily to exposition in non-technical language. It is comparatively easy for a biologist or a physicist to give an account of the root principles of his subject such as can readily be understood by the general reader, though the latter may remain ignorant of the minutiae of the evidence upon which the principles are founded. Chemistry, on the other hand, does not lend itself so well to popular treatment; for this science has evolved a symbolical method of expression of its own which, while to the expert it is more lucid than words, is a stumbling-block to the ordinary man who has not been trained to grasp it. Deprived of its aid, the chemist feels hampered in exposition; and, as a consequence, chemical works designed for the general public are apt to err either in being too elementary in treatment or in taking too much knowledge for granted on the part of the reader.

"In the present volume, it is hoped that these errors have been avoided. No chemical symbols have been employed, and purely elementary questions have not been dealt with at length; so that the non-technical reader will find in the following pages an account of some recent developments in chemistry couched in language which need not present any impediment."

The chapters are entitled: the ramification of chemistry; the allies of chemistry among the sciences; the relations between chemistry and industry; immuno-chemistry and some kindred problems; colloids and the ultra-microscope; the work of the spectroscope; chemistry in space; the inert gases and their place among the elements; radium; niton; transmutation; the nature of the elements; chemical problems of the present and future; the methods of chemical research; the organization of chemical research. Especially interesting paragraphs are to be found on pp. 76, 133, 201, 206, 264.

"It is found that if a rabbit be injected with the blood of a dog the rabbit serum will form a precipitate with the serum of a dog's blood; but, further, it will precipitate also the serum of a fox, which is closely allied to the dog in the biological scale. Again, a rabbit immunized with horse's blood will give a precipitate with the sera of donkeys and tapirs, both of which are closely related to horses. It is evident that this reaction has put into the hand of the biologist a weapon by means of which he can discover the closeness of relationship between various animals; those which are nearly related giving the same response to the test, while those which are in no way connected biologically will give different results. The most interesting result hitherto obtained has been the establishment of the fact that human blood and the blood of the anthropoid apes give a similar reaction, while the blood of some monkeys shows no affinity with the blood of man."

"Cotton, when examining the absorption of dextrocircularly polarized light by copper ammonium tartrate, found that the right- and left-handed tartrates did not possess identical powers of absorption. Now, if light is absorbed by any molecule, some extremely delicate rearrangement of the molecule's internal structure must take place, for it cannot be supposed that a vibration can be stopped without some expenditure of energy. Therefore, in the case of the right- and left-handed forms of copper ammonium tartrate, more energy is being used up by the one form than by the other when light is absorbed, and hence the intra-molecular readjustment is greater in the once case than in the other. In other words, dextrocircularly polarized light is an agent which favors one form of tartaric acid more than another. Now, Byk has pointed out that light is circularly polarized by the surface of the sea, and that one variety of circularly polarized light predominates upon the earth's surface. In this predominance we may find the asymmetric agent foreshadowed by Pasteur, and this agent, so far as the earth is concerned, is practically ubiquitous. It, therefore, seems not improbable that some such cause, acting under favorable conditions, may give rise to a preponderance of a right-handed or left-handed form at one particular period in geological history."

"Instances are actually known, and have been studied spectroscopically within recent years, in which two invisible dark stars collided and flashed into vapor on their impact. Such phenomena put our first assumption out of court; we cannot assume that there is a difference in composition between stars and the nebulae arising from them. What, then, can account for the difference in composition of the stars and the nebulae? Clearly we must conclude that when the elements of the colder stars are raised to the extremes of temperature which exist in the nebulae, the complex elements, such as iron and carbon, disappear as such, and become disintegrated into the simpler substances helium, hydrogen, and other light elements.

"Taking this as a working hypothesis, we shall find that there is a steady increase in the complexity of stellar composition as the stars cool down. Beginning with the early nebulae, we find present only hydrogen and an unknown gas; with the cooling of the nebular mass, as condensation of the gas takes place, helium is formed from the simpler elements; by the time the gaseous material has become consolidated into the form of a hot star, oxygen and nitrogen have come into existence in large quantities; and we can trace the further progress of this synthesis of the elements until at the cooler end of the scale we come to the production of large quantities of carbon in the oldest stars. This hypothesis of stellar evolution is largely due to Sir Norman Lockyer, and it will be seen that it pictures the chemical atoms growing during the cooling of the primal ultra-atomic vapors, just as a visible drop of rain grows by the condensation of invisible particles of water-vapor.

"The evidence from astrophysics, then, tends to make it appear probable that some elements can actually be transmuted into others. Let us next come to the earth's surface and see if we can find any analogous process at work there.

"Ramsay and Cameron's experiments were repeated by Mme. Curie and

Mlle. Gleditsch, who used platinum vessels instead of glass and silica ones; but these investigators found no lithium produced, under these conditions. The negative evidence in such a case can hardly outweigh the positive. It is very hard to get over the fact that when the same solution of copper salt was divided into two portions, one portion which had been treated with niton gave lithium, while the other portion, untreated, showed no trace of the presence of this element, the more so since, as has been mentioned, the glass of the bulbs does not give any trace of lithium when subjected to the action of niton under the same conditions as before."

"From the nature of chemistry, the collaborative method is the favorite one, especially in Germany. There it is usual to find a man who has come into the front rank of science supported by a number of lesser investigators who are ready to place their brains and manipulative dexterity at his disposal in the furtherance of some extensive piece of research. In France, on the other hand, single-handed investigations are more common; while in our own country the two types are not seldom found side by side.

"It is never safe to dogmatize in such matters, but from a practical point of view it appears probable that the coördinated system of research will yield, on the average, a better result with the material which our technical schools and universities are producing. It must be borne in mind that we cannot arrange our conditions entirely with a view to the attainment of the best results if a scientific genius happens to come upon the scene at any moment; such a person only appears at rare intervals in the history of a science, and to plan our research organization solely with the idea of utilizing him to the best advantage when he does come, would be to militate against the success of men who, though they are not geniuses, may yet be far above the ordinary intellectual level of their fellows. A man of the type of Pasteur, when he comes into science, is not hampered by any system which may be in existence; he is capable of utilizing it to the utmost, and of superadding any details which may be necessary for the furtherance of his work.

"The career of a successful investigator may, generally speaking, be divided into four sections. First we find him in his student days acquiring the outlines of the science as a whole and storing up a mass of information which may, at a later date, help him to a true perspective of the field in which he decides to work. Then there springs up in him the desire to advance his subject, to do something which is not already recorded in the literature, and to find out for himself how far the statements which he has read are of universal application. At this point he is generally taken in hand by one of his seniors, and the second stage in his career begins. He is not usually fit at first to undertake an unaided investigation; but he is capable of assisting a more advanced worker; and during this term of apprenticeship he learns the difference between book-knowledge and actual practice. He finds that what on paper seems to be a simple operation really involves immense labor; and he begins to realize how far it is safe to push an inference without running the risk of overshooting the truth. When he has passed through this mill, he has acquired sufficient grip of his subject to admit of his taking up a line of his own, and so he enters the third stage as an investigator. He has now behind him enough work to allow him to feel that he can stand alone; he has gained an experience of methods; and he has acquired a sense of perspective which will prevent him from confusing details with the main principles of the question which he attacks. This period of his scientific life may be long or short, according to his natural ability; if he has little originality, he may never advance beyond this sphere; but if he is a person of exceptional insight he will turn his attention sooner or later to problems of greater and greater importance, until at last in the final phase of his career he may be reckoned among those whose investigations have revolutionized our views in certain fields."

Wilder D. Bancroft

Traité de Physique. *By O. D. Chwolson. Ouvrage traduit sur les Éditions russe et allemande par E. Davaux. Édition revue et considérablement augmentée par l'Auteur, suivie de Notes sur la Physique théorique par E. Cosserat et F. Cosserat. Tome troisième, troisième fascicule. 16 + 15 cm; pp. vi + 260. Paris: A. Herman et Fils, 1912. Price: paper, 9 francs.*—In this volume the author deals with the properties of saturated vapors, including hygrometry; with unsaturated vapors, the critical state, and corresponding states; with heterogeneous equilibrium, including the phase rule and the theory of solutions. In other words, it is physical chemistry from the point of view of the physicist.

On p. 783 the author quotes the work of Schiller as to the increase of the partial pressure of chloroform or ether when in presence of a gas under more than one hundred atmospheres pressure. He rather implies, however, that this increase in partial pressure is due solely to the pressure of the indifferent gas on the surface of the liquid, whereas that would only account for a portion of the increase. It is pretty certain that we are dealing also with a specific solvent action of the compressed gas. It is a little unfortunate, also, to ascribe the theory of dilute solutions to Planck, pp. 912, 931.

On p. 915 the author says: "The wide scope of the phase rule and the diversity of cases to which it is applicable give it a quite exceptional position among physical and chemical laws." After referring to the discussions as to the strict definition of components, the author says, p. 918: "Fortunately the exact definition of the conception of a component has more of a theoretical than a practical importance because it is a very simple matter, in most cases, to tell the number of independently variable substances or components.

Wilder D. Bancroft

Traité de Physique. *By O. D. Chwolson. Ouvrage traduit sur les Éditions russe et allemande par E. Davaux. Deuxième Édition française entierement refondue et considérablement augmentée par l'Auteur, avec des additions et des notes par E. Cosserat et F. Cosserat. Tome premier, premier volume 16 × 25 cm; pp. xviii + 515. Paris: A. Hermann et Fils, 1912. Price: paper, 17 francs.*—In the preface to this new edition the translator says: "M. Chwolson began the publication of his Treatise on Physics in 1897. A German translation by Professor Wiedemann appeared from 1902 to 1908. The French translation, for which M. Amagat wrote an admirable preface, was begun in 1906. In Russia there have been numerous editions: the third edition of the first volume goes back to 1909; that of the second volume to 1911; while a third edition of the third volume will be ready in 1912. The numerous and important additions, made simultaneously in the French and Russian editions, have enabled the work of M. Chwolson to keep its character as a vivid presentation of our actual knowledge. We have now reached a stage, however, both experimentally and theoretically, where so many problems in all branches of physics are taking on so new an aspect that it has become necessary to make a fresh start. M. Chwolson has taken great pains with this delicate task and the reader will see, from the general introduction to this second edition, with what skill the author defines the new point of view from which he is going to write his treatise."

In the general introduction, the author says, p. 9: "In recent years the ideas of the physicists have undergone a remarkable change. The old fundamentals, almost forgotten, have reappeared under new forms. We are actually now (1911) in a period of transition; our previous conceptions of phenomena are more or less obliterated, while the new ones are not yet sharply defined. We are taking part in a desperate struggle between very different and absolutely contradictory views and science hesitates between *one and three fundamentals*. If one includes ordinary matter, one can even say that many scientific men believe in four fundamentals, while others hope that *a single one* will suffice.

"This immense change is the result of the study of the cathode rays, the Roentgen rays, and above all of the radioactive phenomena, with which the names of M. and Mme. Curie will always be identified. We shall discuss these phenomena in detail in the fourth volume. The study of the cathode rays has led to the new doctrine of *electrons*. We have ceased to seek the cause of electrical phenomena solely in the mechanical states of the ether and we have returned to the old views according to which electricity is a definite substance. At first it was merely a question of *negative* electricity to which it was soon found necessary to attribute an atomic constitution. According to the ideas which prevail to-day (1911), negative electricity consists of elementary quantities of substance, of atoms of electricity, which we call *electrons*. An electric current occurs when there is an actual transference of electrons in a conductor. Opinions are divided as to the special properties of the electron and as to whether it can or cannot change in shape; hence it would be premature to lay stress on this point.

"What was previously called *positive* electricity is also looked upon by some scientific men as a definite substance; but there is less agreement as to the structure and properties of positive electricity than in the case of negative electricity.

"As third fundamental we now have the *ether* which fills space and supports and transmits radiant energy (Vol. II). If we add ordinary matter, we have *four* different primordial substances out of which the universe was constructed and by means of which we must account for the infinite variety of physical and chemical phenomena which we encounter. Along with the development of these new conceptions, we have other radical changes in our fundamental physico-chemical hypotheses. The atom of matter was formerly considered as a very small amount of a *homogeneous* substance which could not be divided into smaller particles in any physical or chemical way. Now we attribute to the atom of matter an extremely complex structure in which electrons accompany ordinary matter, the whole forming a system composed of numerous elementary parts which are characterized by different, very rapid, and very complex motions. Under certain conditions the *atom decomposes* and the electrons are scattered, often carrying with them fragments of matter.

"Some scientific men have gone much farther and have also attributed an *atomic structure* to *radiant energy;* they have considered the possibility of atoms of light (elementary quantities of energy), specially in connection with the study of the Roentgen rays.

"The further development of the theory of electrons has had a revolutionary effect along other lines. In order to explain a series of phenomena, to which only reference can be made here, entirely new and very daring views have been put forward in regard to *space and time.* (H. A. Lorentz, Einstein, Minkowski); these are known as the *theory of relativity.* If these ideas should prevail and become perhaps a part of common knowledge, the change in our fundamental conceptions would be so great as to have no equal in history; it would surpass in importance the Copernican revolution.

"We have seen that most people actually recognize four fundamentals: ordinary matter, negative electricity, positive electricity, and ether. Many scientific men, however, do not regard positive electricity as a separate entity; they consider that an atom, which appears to us positively electrified, has merely lost negative electrons. Others believe that we can dispense with ordinary matter and can consider that an atom is merely a system of electrons or a nucleus of positive electricity around which the negative electrons move.

"Recently it has been proposed to take another great step (Campbell, Witte, etc.); *the complete abandonment of the ether.* All the experiments made to show directly phenomena in the ether, at least in a certain way, have hitherto been unsuccessful. This has given rise to the thought that Science might be developed without the conception of the ether; in other words, there is no ether. This point of view leads to the conception of radiant energy (visible light, for instance) as being transmitted in an independent manner through an *absolutely* empty space, perhaps by means of atoms of light. From all this it is clear how uncertain the fundamental beliefs of natural philosophy have now (1911) become; in the near future they may perhaps acquire more simplicity and definiteness. In this work *we shall speak of the ether occasionally but we shall always use the word as referring to space which is not filled with ordinary matter,* and not to space filled with a definite substance."

The second part of this volume deals with mechanics and the titles of the chapters are: motion; force; work and energy; vibratory harmonic motion; transmission of vibrations by radiation; universal gravitation; elements of the theory of the Newtonian potential; weight; dimensions of the physical units. The third part is devoted to a consideration of instruments and methods of measurement.

Wilder D. Bancroft

Handbuch der Mineralchemie. *By C. Doelter. Vol. III: Parts I-II. 18 X 25 cm; pp. 160 (each part). Dresden: Theodor Steinkopff, 1913. Price: 6.50 marks (each part).*—These two numbers deal chiefly with titanium, zirconium, and thorium; but there are a few paragraphs on tin and lead, and the last half of the second part is devoted to columbates, nitrates and phosphates. There is not much of general interest in these two numbers as they are taken up very largely with methods and results of analysis. There seems to be an interesting problem, p. 26, in connection with the genesis of rutile. The synthetic methods involve high temperature; but rutile occurs often in nature under conditions which seem to presuppose low temperature and high pressures as criteria for the formation. The question of the coloring of the zircons, p. 147, is also one that is well worth studying.

There is a rather curious suggestion, p. 244, that the final decomposition product of uranium is not lead but an unknown element having an atomic weight of 206. It was entirely new to the reviewer to find, p. 273, that some people thought that the Chili saltpeter beds were due to the fixation of nitrogen by means of silent electric discharges.

Wilder D. Bancroft

Physical Chemistry and Scientific Thought. *By W. C. Mc. Lewis. 14 × 22; pp. iii + 20. Liverpool: University Press of Liverpool, 1914. Price: 1 shilling.*—This is an inaugural lecture delivered at the University of Liverpool by the Brunner Professor of Physical Chemistry. A few quotations will give some idea of this admirable address:

"It is a characteristic of the truly scientific mind that it is capable of distinguishing, at least in many cases, a real approximate verification, that is a satisfactory verification—and, remember, there are varying degrees of approximation—from false or apparent verification, be it ever so close. The distinction is not infrequently a subtle and, therefore, a difficult one. One has often to weigh many apparently trifling considerations, chance observations, unexpected side effects. One can learn much by experience, but at the same time the experimentalist of the first rank is to a very large measure born, not made.

"I have said that our so-called 'explanations' of chemical and physical phenomena consist in the application of mechanical concepts. It is obvious, therefore, that such explanations are after all partial; but it is not improbable that this is so far as our mental limitations will permit us to go. Although, for example, in that system of logic to which we give the name 'Thermodynamics' an attempt, and a successful one, too, is made to get beyond what might be called the more crude mechanical notions involved in the application of the kinetic theory to the problems of the constitution and behavior of matter, the fact that thermodynamical reasoning simply in virtue of its abstractness has presented great—sometimes very great—barriers to the average intelligence as regards the comprehension of truths even when these have already been put into explicit terms by greater minds—the fact that this difficulty exists is very clear evidence, I think, that our minds are naturally more fitted to adjust themselves to mechanical concepts."

"Research in chemistry and physics may, broadly speaking, be divided into three classes: First, researches in which theoretical considerations and speculations play the entire or at any rate the most important *role*, such as we find, for example, in investigations in mathematical physics and theories of electricity, optics, heat, and capillarity; secondly, researches in which an idea inspired by previous theoretical or experimental results is developed in such a way as to be put more or less conveniently to experimental test. The whole field of physical chemistry may be cited as an illustration of this class. Thirdly, there are researches in which the aim and object is essentially experimental, the interest lying not so much in the theoretical significance of the results themselves as in their usefulness from the standpoint of accumulation of sound experimental data, such as one finds for example in determination of atomic weights and stoichiometric work in general. All these are essential to scientific progress, though I imagine the second is likely to prove the most generally attractive. For the third class, indeed, relatively few are either fitted or willing, as success depends so largely upon innate skill and unwearying patience in view of the somewhat unexciting nature of the work. One must not dogmatise, of course, as to how any investigation is going to turn out—it was, after all, the observation of a slight anomaly in the density of a gas observed by Lord Rayleigh which led in the hands of Ramsay to the discovery of argon and the other members of the rare gas group. Naturally, such divisions as I have mentioned are in actual practice by no means sharply defined. Research in physical chemistry, indeed, progresses along all three, though almost entirely through the medium of the second."

Wilder D. Bancroft

Die radioaktive Strahlung als Gegenstand wahrscheinlichkeitstheoretischer Untersuchungen. *By L. v. Bortkiewicz. 24 × 16 cm; pp. 84. Berlin: Julius Springer. 1913. Price: 4 marks.*—Numerous experiments have been conducted to determine the law of distribution of the time intervals of the emission of particles from a radio-active substance. To compare the various numerical results, it is desirable to analyze them by the methods of the calculus of probabilities. Two methods are possible: either to compare the length of time between two successive scintillations at different stages of the experiment, or to count the number of scintillations in a fixed interval of time. In this volume, no new results are attempted; it is concerned rather with an analysis of the methods of approach, and is simply a mathematical exposition of the principles employed, and the fitting of numercial results of these principles. Both of the above alternatives are considered. Gauss's law of chance is developed, and the result determined by a number of experiments are represented on the same figure with the expectancy curve. A large number of combinations are considered: arithmetic mean, geometric mean, normal dispersion, supernormal dispersion, and subnormal dispersion as well as the possibility of a large number of emissions too feeble to be measured.

The variations of the probability integral made by these assumptions are such that the integrations can not always be performed. In such cases the author not only used Simpson's and Cotes's rule, but carefully shows how algebraic approximations can be employed to still further simplify the processes. The steps are clearly stated, possibly even too much algebraic detail furnished, and each result is set out sharply as such. Apart from a modest list of corrections supplied, the volume is remarkably free from typographical errors.

Virgil Snyder

La Théorie du Rayonnement et les Quanta. *Edited by P. Langevin and M. de Broglie. 25 × 17 cm; pp. 456. Paris: Gauthier-Villars, 1912. Price: 15 francs.*—This volume contains the papers read in November, 1911, at a private congress called at Brussels by Mr. Ernest Solvay. The following papers were presented: The Application to Radiation of the Theorem of the Equal Distribution of Energy, by H. A. Loretz; The Kinetic Theory of the Specific Heat according to Maxwell and Boltzmann, by J. H. Jeans; The Experimental Verification of Planck's Formula for the Radiation from a Black Body, by E. Warburg; The Verification of Planck's Radiation Formula for Rays of Longer Wavelength, by H. Rubens; Law of Black Body Radiation and the Hypothesis of Elementary Quanta, by M. Planck; Kinetic Theory and Experimental Properties of Perfect Gases, by M. Knudsen; Proofs of the Reality of Molecules, by J. Perrin; Application of the Theory of Quanta to Various Physico-chemical Problems, by W. Nernst; Electrical Resistances, by Kamerlingh Onnes; Application of the Theory of Quanta to Aperiodic Molecular Phenomena, by A. Sommerfeld; The Kinetic Theory of Magnetism and the Magnetons, by P. Langevin; The Actual State of the Problem of Specific Heats by A. Einstein.

We are much indebted to Solvay for this collection of papers; but one cannot help being a little disappointed in the discussions. They are extremely perfunctory and it is a great pity that the feeling of being on dress parade should apparently have been predominant. *Wilder D. Bancroft*

Die Theorie der Strahlung und der Quanten. *Edited by A. Eucken. 17 × 25 cm; pp. viii + 405. Halle: Wilhelm Knapp, 1914. Price: 15.60 marks.*—The Bunsen Society has published a German edition of the papers read at the Solvay congress in Brussels (preceding review). The volume also contains an appendix by Eucken on the development of the quantum theory from the time of the congress to the autumn of 1913. The recent development is treated under the heads: foundations of the quantum theory; experimental tests of Planck's formula by radiation measurements; energy content and heat conductance of solids; energy of rotating gas molecules; energy of translation; experimental data bearing on the structure of heat vibration. *Wilder D. Bancroft*

Lecons de Thermodynamique. *By M. Planck. Translated from the third, revised German edition by R. Chevassus. 25 × 17 cm; pp. 308. Paris: A. Hermann et Fils, 1913. Price: 12 francs.*—In the preface the author says: "In this new edition the previous plan and arrangement have been retained. Nevertheless, all the numerical data have been revised and there are also many additions and changes of more or less importance which have been suggested to me by foreign scientific men. I call attention especially to the passages on the law of corresponding states, the definition of molecular weight, the establishment of the second law, characteristic thermodynamic function, the theory of the Joule-Thomson effect, the vaporization of mixed liquids. I shall always receive future criticisms with special gratitude.

"This edition includes the heat theorem established in 1906 by W. Nernst. If this theorem, as now seems possible, is to be verified in all directions, thermodynamics will find itself enriched by a theorem, whose scope would exceed all that we now expect of it both along practical lines and in the field of molecular theory. In order to present this theorem in its elements and in a form best suited to experimental verification, it seems to me necessary to ignore temporarily its significance for atomic theory, since this side of it has never been formulated clearly. This point of view also corresponds with that adopted in the other portions of this book. I have also thought it desirable to give the theorem as broad a form as possible so that the applications would be both simple and general. In doing this I have exceeded to some extent in form and in breadth, the limits imposed by Nernst himself. I mention this fact because the earlier conception of Nernst may still hold even if it proves that the more general form is not correct."

The chapter on Nernst's theorem and on the theory of quanta is a translation of a lecture given before the German Chemical Society in Berlin (16, 187).

Wilder D. Bancroft

Les Idées modernes sur la Constitution de la Matière. *Published by the Société française de Physique. 25 × 17 cm; pp. 370. Paris: Gauthier-Villars, 1913. Price: 13 francs.*—This is a collection of memoirs written for the French Physical Society. The single papers are: Proofs of the Reality of Molecules, by J. Perrin; Grains of Electricity and Electromagnetic Dynamics, by P. Langevin; Elementary Quantities of Energy and Action, by E. Bauer; Electronic Theory of Metals, by E. Bloch; Ionization by Shock and the Electric Spark, by A. Blanc; Ultra-rarefied Gases, by L. Dunoyer; Radiation of Radioactive Substances, by Mme. Curie; Radioactive Transformations by A. Debierne; Magnetic Moments of the Atoms, and the Magneton, by P. Weiss; The Relation of Matter and Ether, by H. Poincaré.

The following paragraph, p. 190, from Bloch's paper on the electronic theory of metals, is interesting. "We have followed the electron theory of metals to the point where it begins to conflict with the experiments on black body radiation. This difficulty is inherent in any theory of electrons as well as in the special electronic theory of metals. It will probably compel us to adjust our ideas so that we may reach a satisfactory compromise; but that is the work of the future. It will not be necessary, however, to throw over the conclusions which we owe to the electronic conception nor the considerable total of phenomena which we have been able to arrange systematically and to account for by means of this conception. In spite of some difficulties of detail, to which we have called special attention, the electron theory brings together in one vast synthesis not only the electrical and thermal conductances and their interrelations, but also the whole of the thermo-electric effects including the laws of electromagnetism and of induction. It also throws some light on the galvano-magnetic phenomena and the mechanism of the radiation of metals. Whatever the future may have in store for it, the theory has brought out relations between certain phenomena which will last. It has shown that it is scarcely necessary to insist on a single mechanism in order to account for the electrical and thermal conductances of conductors. It has proved to be an instrument of great power for investigation and discovery. It will certainly leave a deep mark on all our ideas as to the corpuscular constitution of matter."

Wilder D. Bancroft

Die photographischen Retouche. *By G. Mercator. Third edition. 15 × 22 cm; pp. 74. Halle: Wilhelm Knapp, 1914. Price: 2.50 marks.*—In the preface the author says: "In spite of all attacks, the technique of retouching is essential to the professional photographer. Since it has long been highly developed so far as hand work is concerned, there are no special improvements or important changes to note. The old and tried methods are as important as ever and consequently it has seemed desirable to make the new edition conform as far as possible to the preceding ones. Since opinions differ very much as to the amount of retouching which is desirable, it has seemed undesirable to give illustrations showing the limits of permissible retouching."

One of the most interesting things in the book is the so-called optical retouching, p. 13, whereby a photograph of a building made with a tilted camera is corrected by rephotographing from a tilted transparency or from a tilted paper negative. Special directions are also given for retouching all kinds of prints and for coloring photographs. While the book is primarily intended for the professional, there are a number of passages which are of distinct interest to the amateur. *Wilder D. Bancroft*

Die Misserfolge in der Photographie. *By Hugo Müller. Fourth edition. 15 × 22 cm; pp. 113. Halle: Wilhelm Knapp, 1913. Price: 2 marks.*—The author considers errors due to apparatus, dark room, exposure, development, washing, fixing, drying, intensifying, reducing, varnishing, and retouching, as well as errors liable to occur with films, with instantaneous exposures, with flashlights, and with color-sensitive films or plates. There is also a chapter on the different developers. The book is clear and concise; one can easily see why four editions have been necessary. *Wilder D. Bancroft*

Kapillarchemie und Physiologie. *By H. Freundlich. Second edition. 15 × 22 cm; pp. 5 + 48. Dresden: Theodor Steinkopff, 1914. Price: 1.50 marks.*—The first edition of this pamphlet appeared in 1907, considerably before the author's book entitled *Kapillarchemie*. Instead of rewriting the pamphlet, the author has seen fit to publish it in the original form, apparently on the ground that it is a document. In order to make it of more value, copious notes and comments are introduced in an appendix. The reviewer ventures to think that this is a mistake. It would have been more merciful to the reader to have given him a continuous narrative. In spite of the faulty plan of presentation, the pamphlet is an interesting one. One may not agree with the author in all points but at least he is definite in his statements and one knows where he stands.
Wilder D. Bancroft

Optique physique. *By R. W. Wood. Translated by H. Vigneron and H. Lubrouste. Vol. II, 17 × 25 cm; pp. 478. Paris: Gauthier-Villars, 1914. Price: 18 francs.*—The second English edition was reviewed (15, 707) nearly three years ago. The first volume of the French translation appeared last year (18, 84) and the second (and final) volume is now ready. This volume contains special paragraphs, not in the English edition, on: transmission of radiations of great wave-lengths through thin sheets of silver; experiments of Dunoyer on the fluorescence of sodium vapor: resonance spectra of iodine; polarization of light in the resonance spectra of the vapor of iodine; application of fluorescence as transformer of light. In an appendix the author discusses the radiation of resonance as well as the absorption and diffusion in the vapors of mercury and of sodium. *Wilder D. Bancroft*

THE THEORY OF COLLOID CHEMISTRY[1]

BY WILDER D. BANCROFT

We have dropped Graham's view that a colloidal substance must be amorphous, and we now call a phase colloidal when it is sufficiently subdivided, not committing ourselves definitely as to what degree of subdivision. Colloid chemistry is, therefore, the chemistry of bubbles, drops, grains, films, and filaments. Consequently the differences between colloid chemistry and the chemistry of relatively large masses must be differences arising from the subdivision of a phase or phases. I shall try to make clear that this line of attack leads us to a fairly consistent theory of colloids, a thing which we have not had before.

We begin, as Freundlich has done, with the properties of surfaces. A solid or a liquid surface has the power of adsorbing solids, liquids or gases. The familiar instance of this is the formation of an air film or water film on the surface of glass. We now postulate that surfaces show selective adsorption. This enables us to account qualitatively for all the phenomena of adsorption from solutions including the decomposition. If a substance adsorbs a given base much more readily than a given acid, there will be a tendency for the salt of that base and acid to hydrolyze and for the base to be taken up, leaving the solution acid. The quantitative side of the adsorption is given approximately in simple cases by some form of an exponential formula, the so-called adsorption isotherm. Since we have to have a qualitative theory before we can get a quantitative one, the chief use of the adsorption isotherm for the present is to enable us to tell that a definite compound is not formed. Adsorption is always reversible theoretically, though this is often apparently not true experimentally. If charcoal takes a dye out of solution

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[1] A paper read at the symposium on colloid chemistry during the Montreal meeting of the American Chemical Society.

to such an extent as to decolorize the water practically completely, no amount of washing with pure water will give a colored solution.[1] In such a case the adsorption is strictly reversible and the difficulty was in the interpretation of the results. If the adsorbing substance changes either through agglomeration, crystallization, etc., its specific adsorbing power will change and the adsorbed substance will be held either more firmly or less firmly as the case may be. Either way we get an apparent irreversibility. Both cases are known.[2] The adsorbed substance may also change on standing or on heating, in which case we shall have an apparent irreversibility though we are really dealing, as before, with a new, reversible equilibrium. This case occurs very frequently in dyeing.

It is perfectly familiar to all of us that small drops of a liquid will coalesce to a single large one when brought in contact. It is not familiar to us that solids also coalesce when brought in contact, because solids, as we know them, usually have a film of air on the surface and we do not bring them in contact at all. In fact Cushman and Coggeshall[3] report that in their work a powder which would pass through a 200 mesh sieve surged like a liquid. The film of air was so large relatively to the mass of the particle that they were really dealing with little elastic balls having a hard core. If it were not for the air film, a broken plate could be mended at once by pressing the fragments together.[4] Heating drives out the air film and also tends to make the solid more malleable, so that pressure brings more points in actual contact. We can join two pieces of glass while they are still very viscous and we join two pieces of platinum in the laboratory at temperatures far below the melting point of platinum. The import-

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[1] Freundlich and Neumann: Zeit. phys. Chem., 67, 538 (1909).

[2] Cameron and Patten: Jour. Phys. Chem., 11, 581 (1907); Lottermoser: Zeit. phys. Chem., 62, 377 (1908); Freundlich and Schucht: Ibid., 85, 660 (1913).

[3] Jour. Franklin Inst., 174, 672 (1912).

[4] Cf. Brewer: Kitte und Klebstoffe, 24 (1907).

ance of clean surfaces when soldering is well known. We can electroplate copper on copper without difficulty because we can keep a clean surface. To plate an adherent deposit of nickel on nickel requires special precautions; and it is a much more difficult matter to get an adherent deposit of gold or silver upon aluminum.

We, therefore, conclude that solid grains or liquid drops will agglomerate if actually brought into contact and that to keep them from doing so we must have a surface film of some sort. Since this agglomeration takes place spontaneously, work must be done on the liquid or solid to disintegrate it. It is easy to see also that a film might keep drops separated and yet not break up a large drop into a lot of smaller ones. Dirty mercury will remain as a single liquid mass indefinitely so far as we know. If we disintegrate the mass by shaking, a film will form over each drop and will keep the drops from coalescing. It is also easy to see that less work will be necessary to disintegrate the mercury in case we add something which lowers the surface tension of the mercury. In some cases we get disintegration very easily. Water will disintegrate gelatine at about 30°; but cellulose only at very much higher temperatures. The disintegrating action of water on metals is negligible except under special conditions.[1] Except with such substances as gelatine we have to use special methods of disintegration, and the presence of a suitable surface film of some sort is necessary to prevent the liquid drops or solid particles from coalescing again.

If we drop a stone into water, it sinks very rapidly; if we grind the stone into coarse particles these sink less rapidly; if we grind the stone into fine particles, these sink slowly; if we grind the stone into very fine particles we should expect them to sink very slowly, the rate being a function of the diameter of the particles. This is not the case, however. Very fine particles do not follow Stokes' equation and do not

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[1] Mengarini and Scala: Zeit. Kolloidchemie, 6, 65, 240 (1910); 10, 113 (1912).

settle at all, because of the Brownian movements which are negligible for coarse particles. We, therefore, conclude that any substance can be brought into a state of colloidal solution provided we make the particles of that phase so small that the Brownian movements will keep the particles suspended, and provided we prevent agglomeration of the particles by a suitable surface film. Coalescence may be prevented by a non-electrical film, by an electrical film (electrical charge) or by any combination of the two. Non-electrical suspensions are due to marked adsorption of substances in true solution together with a suitable change of surface tension—to be discussed under peptonization—or to the adsorption of a colloid which is readily peptonized by water, a protecting colloid so-called. It is not proper to assume, as Freundlich[1] does, that all adsorption is accompanied by a lowering of the surface tension. Freundlich bases his conclusions on the Gibbs' formula which applies to a homogeneous solution and not to the case of adsorption at all. An electrical suspension is due to the preferential adsorption of some ion. So long as the particles are all charged positively or all negatively they will repel each other and will not coalesce. Neutralization of the charge causes precipitation through agglomeration.

On this statement of facts there is no apparent reason why one should not make a colloidal solution of any substance of almost any desired concentration. Practically, we cannot do this, though we can vary the concentration within limits by changing the protecting colloid. Also, we know that people determined the solubility of tannin in water when they thought that it really dissolved. We know now that tannin only appears to dissolve in water; but a change in our theoretical views cannot change the facts, though it may change our interpretation of them. I, therefore, conclude that there is a limiting concentration beyond which the peptonizing action of the liquid and the protective action of the surface film cease to be effective and that we consequently get an apparently

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[1] Kapillarchemie, 52 (1909).

definite solubility which, of course, varies with the size of the particles. In fact, I suspect that a number of solubility determinations on such things as the so-called calcium sucrates will turn out to have been really a study of colloidal solutions. In view of what we know in regard to the behavior of the cellulose nitrates with mixed solvents, I doubt whether Oudemanns[1] determined the true solubility of cinchonine in alcoholic chloroform.

If we start with two liquids, either can be dispersed in the other and the question of which constitutes the internal phase depends entirely on the nature of the protecting film. For an emulsion to be possible the third substance must pass into the surface separating the liquids[2] and must possess the power of forming a coherent film in presence of the two liquids. Let *A* be one liquid, *B* the other, and *C* the protecting film. If the surface tension of *C* is lower on the side towards *B*, liquid *B* will tend to form the internal phase, while liquid *A* will tend to form the internal phase if the reverse be true.[3] This has been realized experimentally in a number of cases.[4] With a sodium soap, oil becomes the internal phase and water the external one, while the reverse is true with a calcium or magnesium soap. Rosin enables one to emulsify large amounts of water in linseed oil.

The study of emulsions throws light on the more difficult question of peptonization. Doyle[5] found that iodine was adsorbed readily by charcoal or graphite and yet had very little effect in preventing sedimentation, while other substances were adsorbed strongly and had a marked effect in preventing sedimentation. Consequently adsorption of two different substances may act in fundamentally different ways. This is true irrespective of whether any or all of the three substances are or are not electrolytes. As yet there are no experimental

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[1] Zeit. anal. Chem., 11, 287 (1872).

[2] Hofmann: Zeit. phys. Chem., 83, 385 (1913).

[3] Bancroft: Jour. Phys. Chem., 17, 515 (1913).

[4] Newman: Ibid., 18, 34 (1914).

[5] Jour. Phys. Chem., 17, 390 (1913).

data on this point; but it seems probable that a relatively low surface tension on the water side of the adsorbed film and a relatively high surface tension on the side towards the solid will make the film curl so as to tend to peptonize the solid as internal phase. If the reverse is the case the solid will tend to become the external phase. Neither tendency will prevail if the two surface tensions are practically equal. I hope to test this before long with pyroxylin and mixed solvents.

All methods for preparing colloidal solutions can be classified either as condensation or as dispersion methods. Condensation methods involve precipitation as finely divided particles and suitable strong adsorption (including protecting colloids) or precipitating agents kept low either by suitable choice of reagents or by dilution. Dispersion methods involve the washing out of precipitating agents (effective only so long as particles are finely divided), the addition of a peptonizing agent (suitable strong adsorption), or disintegration by electrical, mechanical, or other means in the absence of a precipitating agent or in the presence of a protecting agent.

The properties of colloids with water as external phase follow readily from the theory outlined. If the suspended particles are practically insoluble, there will be no change of surface tension, no osmotic pressure and no diffusion except what is due to the Brownian movements. If the particles are slightly soluble, there will be a slight change of surface tension, some osmotic pressure, and some diffusion other than that due to the Brownian movements. In so far as the colloids are electrical suspensions, they will move to the cathode or anode, depending on whether they adsorb a cation or anion preferentially. Since we are dealing throughout with selective adsorption, we see that at best it can only be a first approximation to group all univalent cations together and all bivalent cations, etc. As a matter of fact, the data cited by Freundlich[1] to show the desirability of such a grouping constitute a still stronger argument against it. The data of

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[1] Kapillarchemie, 351, 352, 367 (1909).

Pappadà[1] show that one must discriminate between the different alkali metals. We have always put hydrogen and hydroxyl ions in a separate class because it was quite impossible to group them with the other univalent ions. Potassium and nitrate ions do not peptonize silver bromide perceptibly; but silver and bromine ions do. The moment we consider the matter as one of selective adsorption, we see that one cannot ignore the nature of the anions in solution when we are dealing with a negatively charged particle. We have been misled by an injudicious selection of salts. As I pointed out at the Cincinnati meeting, the theory of selective adsorption enables us to predict the reversal of the effects of the anions on the stability of albumin when one changes from a slightly alkaline to a slightly acid solution.

Positive and negative colloids will, of course, precipitate each other when in proper relative proportions, and provided adsorption takes place. These precipitates may be peptonized as such under suitable conditions and may then easily be mistaken for compounds. The lakes are one instance of this and I imagine that aluminum silicate is another, when precipitated in the wet way.

Since any substance may be converted into a colloidal suspension by being subdivided sufficiently,[2] it follows that we may have any number of different colloidal solutions of the same thing if we start, for instance, with ferric oxide or aluminum oxide having different amounts of water in the particles. As a matter of fact we have recognized for years at least two different colloidal iron oxides and colloidal aluminas. Nobody knows what we have in the case of the cellulose nitrates. If a precipitated suspension agglomerates on standing, it will not peptonize with the same readiness as before or with the same concentration of peptonizing agent. If the agglomeration is accompanied, as it often is, by a change in water content, we have two variables each of which may have a marked

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[1] Zeit. Kolloidchemie, 4, 214 (1909); 6, 83 (1910); 9, 136 (1911).

[2] Cf. Wegelin: Zeit. Kolloidchemie, 14, 65 (1914).

effect on the peptonization or apparent solubility. Many instances of this are known especially with sulphides and hydroxides so-called (including silicic acid).

No distinction has been made thus far between colloidal suspensions and colloidal solutions[1] because I believe that this distinction is an unsound one though I recognized the usefulness of it at the time it was made. While we are reasonably sure that colloidal gold is a solid and that colloidal oil is a liquid, the two behave exactly alike when both are suspended electrically.[2] There is no apparent reason why we should put hydrous ferric oxide on one side of the line and hydrous stannic oxide on the other. I fail to see any fundamental difference between a chromic oxide jelly and a silicic oxide jelly. Consequently, I believe that we should drop the terms of suspension colloids and emulsion colloids, which are now a hindrance and not a help. On the other hand, there is a difference between a colloidal solution in which the more mobile phase (usually water) is external phase and one in which the water is internal phase.

I have already pointed out the properties of colloidal solutions with water as external phase and I will now take up the case where the more mobile phase is internal. We must have a honeycomb structure and we may, therefore, get a distinct change in surface tension and in viscosity, In so far as the less mobile phase is practically insoluble in the other we shall get no appreciable osmotic pressure. We get these phenomena to a marked degree with gelatine and I conclude that gelatine is usually the external phase in a so-called aqueous solution of gelatine.[3] These two types, which correspond to a certain extent to the suspension colloids and emulsion colloids, are not to be considered as hard and fast things. We can change from an emulsion of oil in water to one of water in oil by changing the nature of the third component. Under

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[1] Noyes: Jour. Am. Chem. Soc., 27, 85 (1905).

[2] Ellis: Zeit. phys. Chem., 80, 597 (1912).

[3] This was first suggested to me by Mr. T. R. Briggs three or four years ago.

peptonization we saw that one adsorbed substance tends to peptonize the solid as external phase and another as internal phase. It might be very difficult to find a substance that would peptonize gold as external phase in water; but there should be no difficulty in changing from one type to the other if we took less extreme cases. Concentrated sodium sulphate solution flocculates gelatine instead of making it set to a jelly and we can get hydrous ferric oxide coming down either as unquestionably internal phase or as a jelly in which it probably is external phase. Since some of the colloids which form the external phase are readily dispersed by water (gelatine for instance), the solutions are fairly stable. All gradations are known, however.

Jellies may have a honeycomb structure, in which case the water is internal phase and the gelatinous matter constitutes the external one; or it may have a sponge structure. It is usually assumed that in this latter case the water is the external phase, apparently because a sponge can be immersed completely in water. A moment's thought will show, however, that there is neither external nor internal phase. Each phase is continuous and neither is dispersed in the other. This will be seen a little more clearly perhaps if we consider a roll of wire fence standing out-doors. The fence is continuous and, therefore, is not the dispersed phase; but exactly the same is true about the air. The general opinion seems to be that most jellies are of the sponge type and are formed by the coagulation and partial coalescence of a dispersed phase.[1] I doubt the accuracy of the conclusion. In the benzene-water and oil-water jellies, we know that we have a honeycomb structure. Wet sand would be a sponge structure if the grains of sand could be made to unite at the edges. Actually it is a case of water as the external phase. A brick is a solid-and-vapor jelly of the sponge type.

It is quite evident that a solution having a honeycomb

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[1] Zsigmondy: Zeit. anorg. Chem., 71, 356 (1911); Bachmann: Ibid., 73, 125 (1912); Flade: Zeit. phys. Chem., 82, 173 (1913).

structure can change readily into a jelly; but I do not see how a solution with gelatinous particles suspended in it can become a jelly without leaving a liquid layer. It seems to me possible to have a liquid layer formed when we have a honeycomb jelly; but that we must have a honeycomb jelly whenever there is no liquid layer formed. If a honeycomb jelly retains its flexibility of walls while drying, it will dry to a varnish. If the partially dried jelly takes up water again, it will swell. I can see how a honeycomb jelly can swell in water without being disintegrated, because the collapsed cells fill with water;[1] but I do not believe that a sponge jelly can do this to any appreciable extent.

In the foregoing outline of a working theory of colloid chemistry only four postulates have been made, and the first three of these will be accepted by everybody without any hesitation.

1. Colloid chemistry differs from ordinary chemistry only through the variations resulting from the increasing dispersity of one or more phases.
2. Selective adsorption takes place at surfaces.
3. Sufficiently finely divided particles, which are prevented from coalescing, will be kept suspended in a medium by the Brownian movements.
4. Under fixed conditions of peptonization we get an approximately definite limiting concentration corresponding to a saturated solution in the case of a true solution.

Cornell University

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[1] Bancroft: Jour. Phys. Chem., 16, 395 (1912).

ON THE EXISTENCE OF COMPOUNDS IN BINARY LIQUID MIXTURES

BY J. HOWARD MATHEWS AND RAYMOND D. COOKE

In recent years much work has appeared concerning the question of the interpretation of viscosity maxima in binary mixtures as indicative of the presence of chemical combinations of the two liquids. As early as 1847 Poiseuille[26] noticed that the viscosity of mixtures of ethyl alcohol and water was much greater than that calculated by the rule of mixtures. Instead of being a straight line the curve exhibited a decided maximum which occurred at a concentration corresponding to the equimolecular quantities of the alcohol and water. In 1861 Graham[16] observed the same phenomenon and reported several similar cases among which were mineral and organic acids and aliphatic alcohols in water. Wijkander[69] in 1878 found that acetic acid and water had a maximum viscosity at a composition corresponding to equimolecular quantities but that this maximum was shifted at different temperatures, and as the temperature was raised the curve became more flat. In recent years Varenne and Godeffroy[67] studied the irregularities in the curve for alcohol and water and claimed to detect no less than five hydrates; and in a mixture of alcohol and acetone as many compounds of these two. In 1912 Denison[124] pointed out that the actual maximum in a curve is not of any significance but that the point to be considered is the point which lies farthest from the straight line. At this point the effect of mixing the liquids is the greatest. He also showed that while the points of maximum viscosity shift with the temperature, this point of greatest deviation does not. The present status of the theory that deviations in viscosity are due to the presence of a compound is as follows: In case a third substance is present in the mixture, and if this substance has a viscosity widely different from that of either of the components, the greatest deviation from the straight line will be experienced when there is a maximum amount of the third substance present. It will be seen that this maximum amount will be present when the total composition of the mixture is the same as that of the compound, for if an excess of either were present it would change the equilibrium and dilute the compound leaving a smaller relative amount. There are indeed other forces which will affect the viscosity of a mixture so that the point of maximum distance from the straight line does not always represent a simple empirical formula, but in general it is assumed that where there is a decided maximum in the curve a compound, either simple or complex, is present. It is the purpose of this paper to present an entirely new line of evidence which leads to the same conclusion.

A recent paper by Batschinskii[1] shows some interesting relationships concerning the change of velocity of pure liquids with the temperature. Without going greatly into detail in his work we may say that he gives several formulae which have been proposed from time to time to connect the viscosity of liquids with the temperature, and shows that they have not been entirely successful. Instead of using the temperature as one of the independent variables he uses the specific volume of the liquid, reasoning from the assumption that viscosity is due to friction between the molecules and therefore varies as the distance between the molecules. The equation would then stand:

$$\text{Viscosity} = \frac{\text{Const}}{v}$$

where v is the specific volume. Here, however, when the viscosity is infinite, a physically realizable condition, the volume would have to be zero, which is impossible. By introducing a correction for the volume of the molecule similar to that in the gas law this objection is avoided. If instead of the specific volume we use the difference between the specific volume and a constant ∞ we obtain:

$$\text{Viscosity } (\eta) = \frac{c}{v - \infty}$$

where c is another constant. By a simple transposition we get

$$v = \infty + \frac{c}{\eta}$$

Here the specific volume is a linear function of the fluidity or $\frac{1}{\eta}$ and the equation lends itself readily to graphic proof. If a liquid follows this rule, plotting the fluidity against the specific volume should result in a straight line. The constant ∞ is obtained graphically and is the intercept of the line with the volume axis. Physically it is the specific volume at infinite viscosity and is equal to the average of the volumes of the solid and liquid substances at the freezing point. The constant c is the tangent of the angle made by the line and the fluidity axis and is nearly the same for all liquids, ranging from 0.000331 to 0.000647.

Batschinskii applied this formula to eighty-seven liquids, the data for which were obtained from the work of Thorpe and Rodger.[27] In all cases of non-associated liquids the equation applied. The lines obtained were perfectly straight and the values for viscosity obtained experimentally and those calculated from the equation agreed in all cases within one percent. With associated liquids, however, mainly the organic acids and aliphatic alcohols, the curves were distinctly concave toward the fluidity axis and the equation did not apply.

All the pure associated liquids which have been studied give curved lines, and since this has been demonstrated for a large number of substances it may be taken as a fair criterion of association. We have conducted experiments to see if the same is true in such liquid *mixtures* as are generally assumed to be associated, and we find this to be the case as the following experiments show.

For the purpose of this work twenty-four pairs of liquids were chosen, the viscosity isotherms for each pair of which had been worked out by the previous investigators, as indicated below. These isotherms fall into two distinct classes, first those which exhibit a decided maximum, into which class nine of the pairs fall; and those in which the intermediate values fall between those of the pure components, to which the other fifteen belong. In the former class the ratio chosen for experiment was that composition which shows the greatest deviation from the straight line, that is the proportion in which the effect of mixing has been to produce the greatest difference between the observed values and those calculated from the admixture rule. To this class belong:

Acetic acid-aniline[45]	56-44 percent
Methyl alcohol-water[36]	36-64 percent
Propyl alcohol-water[38]	50-50 percent
Water-acetic acid[36]	22-78 percent
Water-pyridine[45]	33-67 percent
Acetic acid-pyridine[45]	77-23 percent
Ethyl alcohol-water[36]	45-55 percent
Chloral-water[55]	88-12 percent
Chloral-ethyl alcohol[55]	74.3-25.7 percent

In the second class the mixtures were made uniformly 50 percent of each component and comprised the following pairs:

Toluol-benzol[58]
Carbon tetrachloride-chloroform[58]
Nitrobenzene-ethyl acetate[58]
Acetic acid-acetone[45]
Aniline-acetone[45]
Chloroform-benzol[58]
Carbon tetrachloride-benzol[64]
Nitrobenzene-benzol[58]
Acetone-ethyl alcohol[36]
Ethyl acetate-benzol[36]
Ethyl alcohol-benzol[58]
Pyridine-aniline[45]
Pyridine-ethyl acetate
Ethyl alcohol-ethyl acetate
Ethyl alcohol-methyl acetate

The shapes of the viscosity isotherms for all of these pairs, copied from the curves or plotted from the data in the literature, are shown in Figs. I and II.

Purification of liquids;

Benzol was purified by freezing a considerable amount several times, drawing off the liquid portion after each freezing.

Toluol was prepared by distillation from phosphorus pentoxide, b. p. 109.5° at 740 mm.

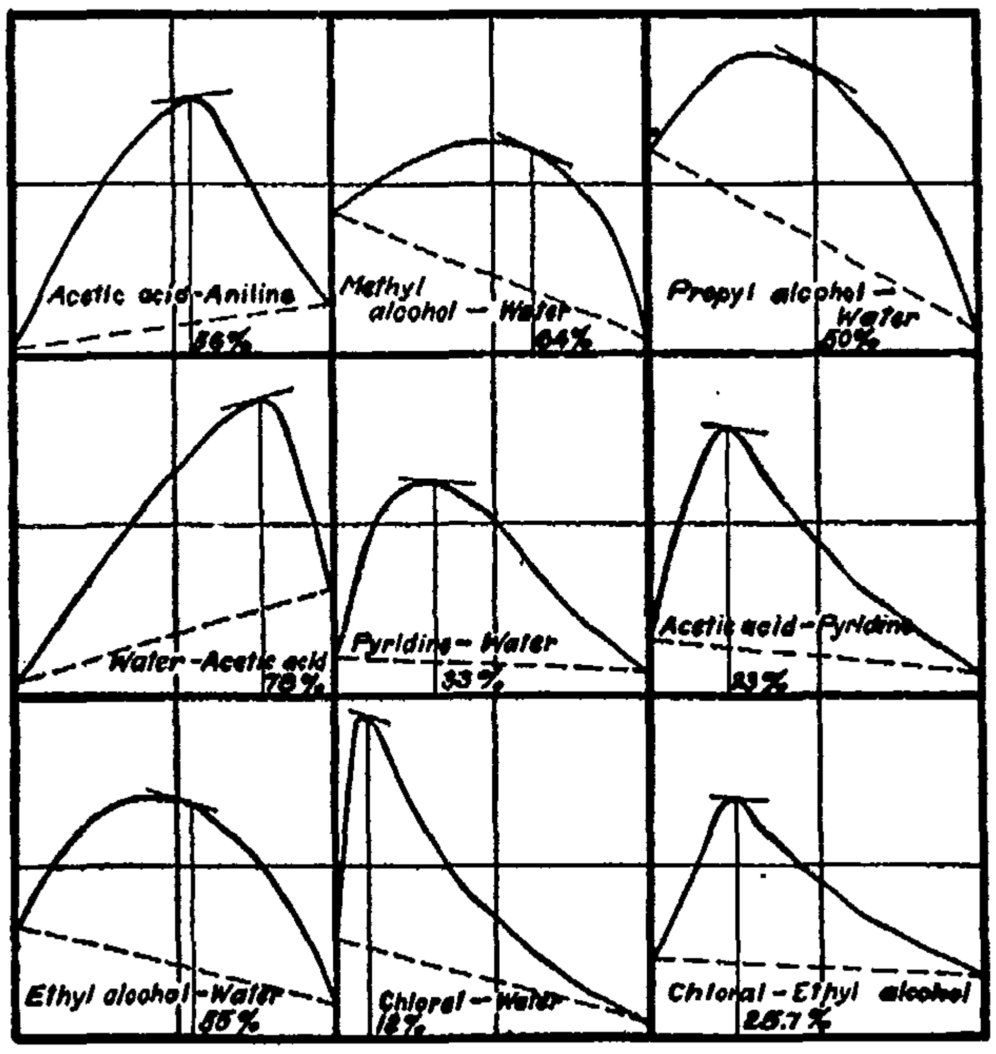

Fig. I[1]

Methyl, ethyl, and propyl alcohols and acetone were dried for several days over anhydrous copper sulfate and distilled.

Methyl alcohol, boiling point 65°-65.5° at 745 mm.

Ethyl alcohol, boiling point, 78°-78.2° at 745 mm.

Propyl alcohol, boiling point, 97° at 745 mm.

Acetone, boiling point, 56°-56.5° at 750 mm.

Acetic acid was frozen several times in the same way as benzol.

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[1] In Figs. I and II the curves are not drawn to the same scale. They are reproduced here merely to show the general form of such curves.

Chloroform was distilled from phosphorus pentoxide. Boiling point, 60.5°–61° at 730 mm.

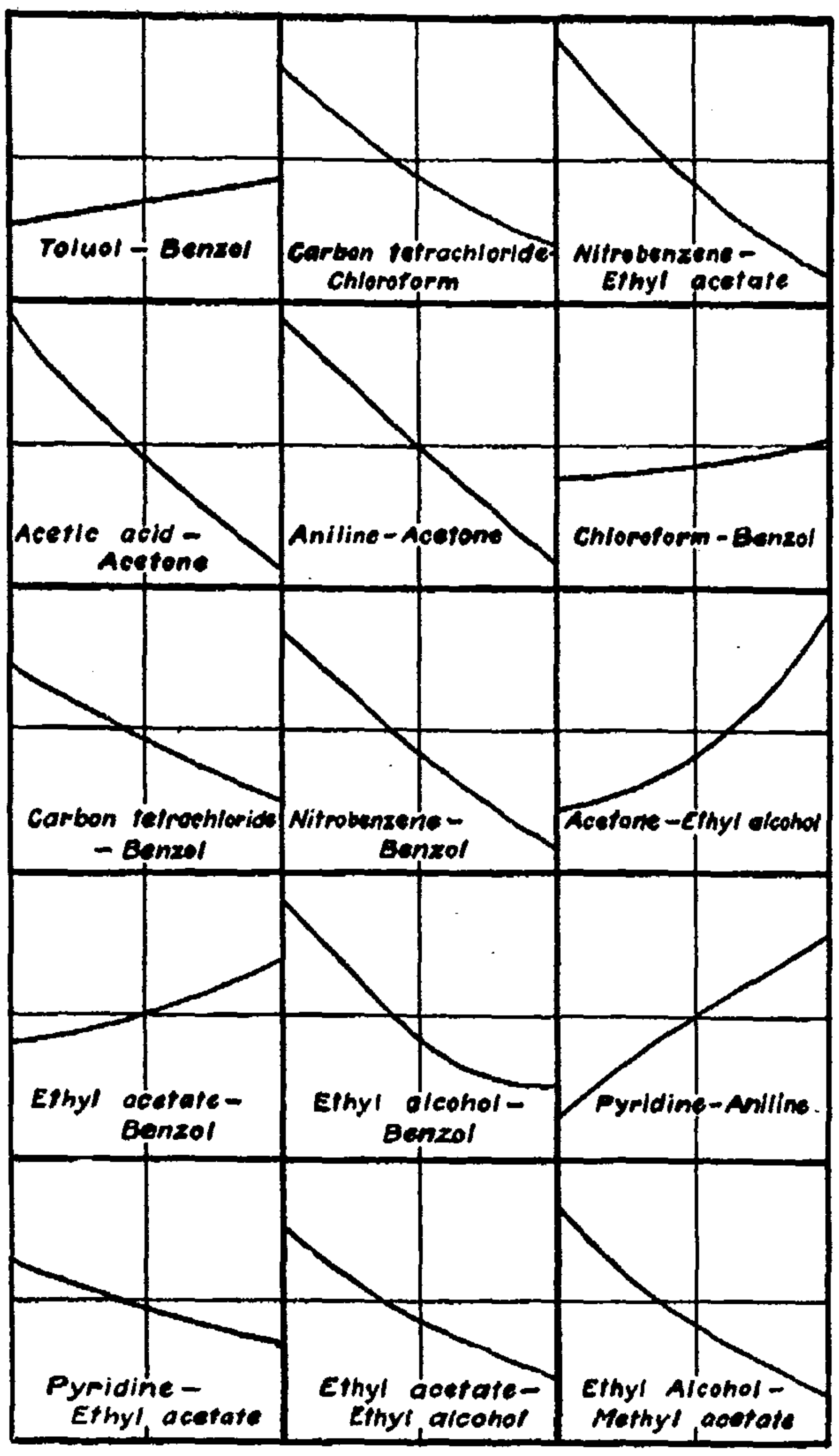

Fig. II

Pyridine was dried several days over solid KOH, digested with potassium permanganate and finally distilled from barium oxide, boiling point, 114° at 748 mm.

The samples of ethyl and methyl acetates at hand were found to contain considerable amounts of alcohol. They were shaken several times with saturated calcium chloride solution to remove the alcohol, dried over anhydrous calcium chloride and finally distilled twice from phosphorus pentoxide.

Ethyl acetate, boiling point, 75°–76° at 735 mm.

Methyl acetate, boiling point, 55°–56° at 740 mm.

Nitrobenzene was distilled and the greater part, boiling 205.8°–206.1° at 740 mm., was collected.

Carbon tetrachloride was dried for several days over anhydrous calcium chloride and distilled from freshly ignited calcium chloride, boiling point 76°–77° at 735 mm.

Aniline was redistilled. Boiling point 183°–184° at 750 mm.

The water used was distilled from a large copper still and approximately the middle third of the distillate was collected for use.

The mixtures were all made up by weight in small glass stoppered bottles holding about 125 cc, and were kept carefully stoppered except when samples were being taken. The measurements at zero degrees were made in a large battery jar filled with cracked ice and water and surrounded with asbestos. No change in temperature could be observed with a thermometer capable of being read to 0.01°.

At the higher temperatures, namely 25°, 40°, 55°, and 70°, a glass thermostat was used. It was heated by means of a Simplex electric heating coil immersed in it, the heating element being controlled by a toluene regulator and relay. It was kept thoroughly stirred at all times when measurements were being made and at the higher temperatures the jar was surrounded with asbestos to prevent excessive radiation. Thermometers standardized by the U. S. Bureau of Standards and reading to one twentieth of a degree were used and the maximum deviation in the temperature was never greater than one-tenth of a degree.

The viscosimeter used was a modified form of the Ostwald type, being provided with means for admitting only dry air and not being opened to the air during the time the measurements were being made. This was necessary on account of the fact that many of the liquids were quite hygroscopic. Five cc of the liquid were admitted to the cleaned and dried viscosimeter from a pipette and when sufficient time had been allowed for the liquid to attain the temperature of the bath five to ten determinations of the time required for the liquid to flow out of the bulb were made and the average of these used in the calculations. After each measurement the instrument was rinsed out with alcohol and redistilled ether, and dried by drawing a slow current of air through it. The densities were measured with an Ostwald-Sprengel pycnometer of 13 cc capacity.

With the exception of the pairs, Chloral-Water, Chloral-Alcohol, and Pyridine-Aniline the data given below were gotten by us. The data on the first two are taken from Kurnakow and Efremow[56] and the last from Faust[45].

The following tables give the observed fluidities and specific volumes of the mixtures named, and in those of the second class the values are given for the fluidities calculated from Batschinskii's equation, and the differences.

ACETIC ACID-ANILINE 56–44 PERCENT

Temp.	v	f
25	0.92398	5.49
40	0.93816	12.78
55	0.95243	23.87
70	0.96772	38.39

METHYL ALCOHOL-WATER 36–64 PERCENT

Temp.	v	f
0	1.0490	27.31
25	1.0651	63.12
40	1.0757	96.13
55	1.0882	131.8
70	1.1015	173.0

PROPYL ALCOHOL-WATER 50–50 PERCENT

Temp.	v	f
0	1.0824	13.23
25	1.1040	37.20
40	1.1180	61.48
55	1.1326	88.18
70	1.1493	119.7

WATER-ACETIC ACID 22–78 PERCENT

Temp.	v	f
0	0.91848	19.75
25	0.93967	42.87
40	0.95295	63.73
55	0.96660	85.05
70	0.98148	109.0

WATER-PYRIDINE 33–67 PERCENT

Temp.	v	f
0	0.97772	17.55
25	0.99926	43.85
40	1.0131	68.03
55	1.0274	95.02
70	1.0429	126.2

ACETIC ACID-PYRIDINE 77–23 PERCENT

Temp.	v	f
0	0.90618	7.79
25	0.92718	20.55
40	0.94392	33.68
55	0.95878	48.25
70	0.97515	65.50

ETHYL ALCOHOL-WATER 45–55 PERCENT

Temp.	v	f
0	1.0539	14.42
25	1.0742	42.37
40	1.0894	70.56
55	1.1028	103.2
70	1.1181	145.0

CHLORAL-WATER 88-12 PERCENT

Temp.	v	f
50	0.61863	5.75
60	0.62777	11.13
70	0.63837	19.95
85	0.65364	37.69
90	0.66080	48.61

CHLORAL-ETHYL ALCOHOL 74.3-25.7 PERCENT

Temp.	v	f
40	0.73910	21.02
45	0.74367	25.95
50	0.74973	31.24
60	0.75706	43.20
70	0.76668	58.65
85	0.78082	84.32

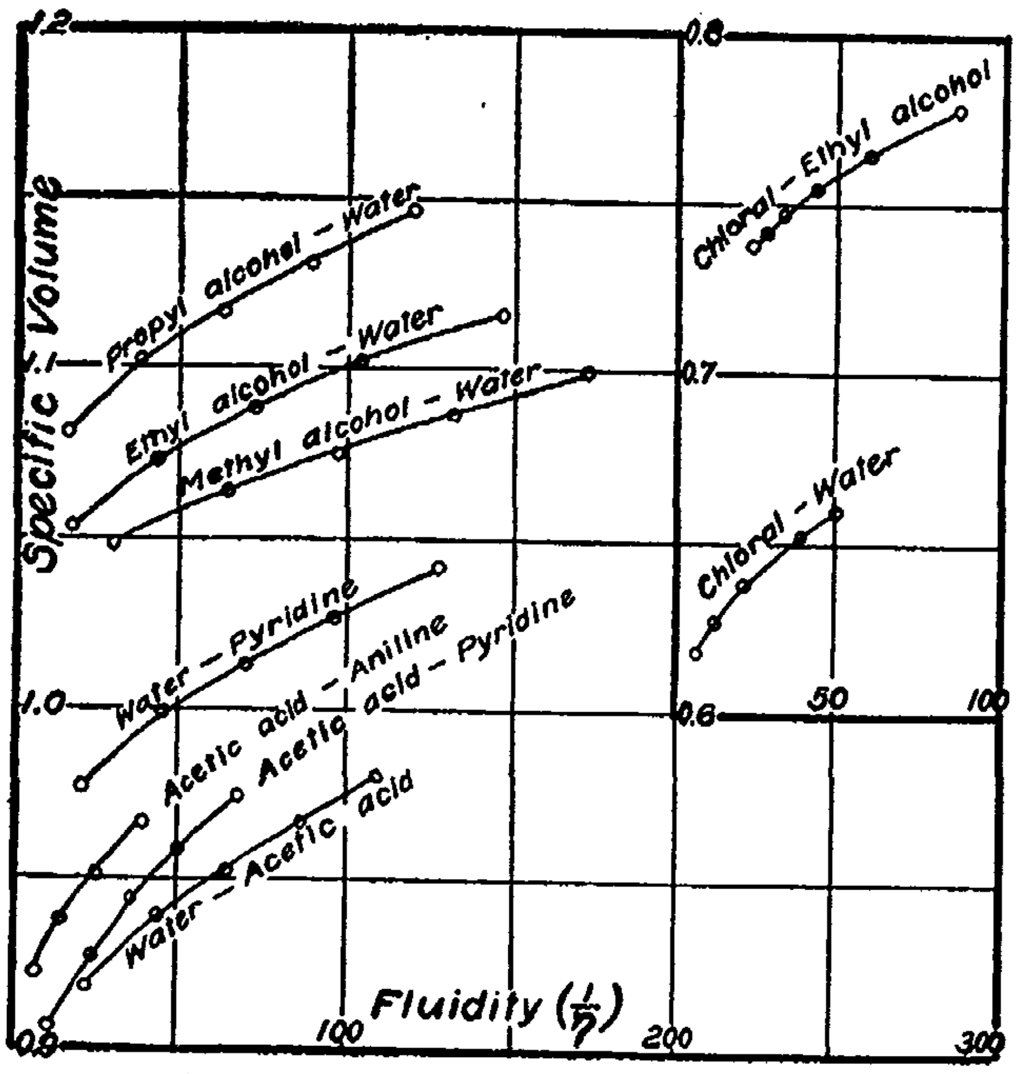

Fig. III

The curves obtained by plotting the above tabulated values as done by Batschinskii are shown in Fig. III. It will be seen that they are all distinctly concave to the fluidity axis as were those obtained from data on associated pure liquids. In the second class are the following:

TOLUOL-BENZOL c = 0.000602 ∞ = 1.0475

Temp.	v	f obs.	f calc.	Diff.
0	1.1222	124.4	124.2	—0.2
25	1.1545	179.5	177.8	—0.7
40	1.1748	216.6	211.9	—4.7
55	1.1958	249.3	247.0	—2.3
70	1.2184	284.3	284.3	0.0

CARBON TETRACHLORIDE-CHLOROFORM c = 0.000520 ∞ = 0.5750

Temp.	v	f obs.	f calc.	Diff.
0	0.63640	116.8	118.2	1.4
25	0.65660	153.8	156.9	3.1
40	0.66907	183.5	181.0	—2.5
55	0.68245	206.6	206.6	0.0

NITROBENZENE-ETHYL ACETATE c = 0.000643 ∞ = 0.8910

Temp.	v	f obs.	f calc.	Diff.
0	0.94528	84.02	84.4	0.38
25	0.97060	122.6	123.8	1.2
40	0.98672	153.8	149	—4.8
55	1.0030	179.3	174.3	—5.0
70	1.0213	202.9	202.5	—0.4

ACETIC ACID-ACETONE c = 0.000651 ∞ = 0.9985

Temp.	v	f obs.	f calc.	Diff.
0	1.0681	104.1	105.2	1.1
25	1.1011	150.1	155.2	5.1
40	1.1215	187.6	186.3	—1.3
55	1.1430	219.7	218.8	—0.9
70	1.1662	250.8	253.7	2.9

Aniline-Acetone $c = 0.000648$ $\infty = 1.026$

Temp.	v	f obs.	f calc.	Diff.
0	1.0722	70.3	71.4	1.1
25	1.1002	113.4	114.6	1.2
40	1.1221	146.7	148.3	1.6
55	1.1400	176.5	176.0	—0.5
70	1.1590	205.2	205.2	0.0

Chloroform-Benzol $c = 0.000547$ $\infty = 0.8170$

Temp.	v	f obs.	f calc.	Diff.
0	0.88626	127.2	126.7	—0.5
25	0.91242	176.2	174.5	—1.7
40	0.93068	210.5	207.8	—2.7
55	0.94940	241.8	242.3	0.5
70	0.96718	275.9	274.9	0.0

Carbon Tetrachloride-Benzol $c = 0.000518$ $\infty = 0.8125$

Temp.	v	f obs.	f calc.	Diff.
0	0.86264	97.12	96.7	—0.4
25	0.88930	144.2	148.3	4.1
40	0.90634	181.8	181.1	—0.7
55	0.92370	212.8	214.8	2.0

Nitrobenzene-Benzol $c = 0.000620$ $\infty = 0.9155$

Temp.	v	f obs.	f calc.	Diff.
0	0.96267	76.91	76.1	—0.8
25	0.98766	114.3	116.3	2.0
40	1.0027	142.8	140.6	—2.2
55	1.0175	166.3	164.5	—1.8
70	1.0344	192.0	191.8	—0.2

Acetone-Ethyl Alcohol $c = 0.000617$ $\infty = 1.1360$

Temp.	v	f obs.	f calc.	Diff.
0	1.2169	129.9	130.9	1.0
25	1.2554	189.0	192.8	3.8
40	1.2827	237.9	237.9	0.0

Ethyl Acetate-benzol $c = 0.000568$ $\infty = 1.0140$

Temp.	v	f obs.	f calc.	Diff.
0	1.0984	149.3	148.5	—1.2
25	1.1333	206.6	210.0	3.4
40	1.1556	251.2	249.6	—1.6
55	1.1783	289.5	289.5	0.0

Ethyl Alcohol-benzol $c = 0.000608$ $\infty = 1.1130$

Temp.	v	f obs.	f calc.	Diff.
0	1.1558	70.71	70.3	—0.4
25	1.1899	121.9	126.4	4.5
40	1.2117	161.3	162.0	0.7
55	1.2356	201.5	201.5	0.0

Pyridine-aniline

Temp.	v	f obs.	f calc.	Diff.
0	0.9756	27.7	—	—
19	0.9930	48.8	—	—
58.6	1.027	105.0	—	—
100	1.068	200.0	—	—

Pyridine-ethyl Acetate $c = 0.000713$ $\infty = 0.9570$

Temp.	v	f obs.	f calc.	Diff.
0	1.0446	122.0	122.9	0.9
25	1.0744	170.0	164.8	—5.2
40	1.0932	194.0	191.0	—3.0
55	1.1131	219.2	218.8	—0.4

Ethyl Alcohol-ethyl Acetate $c = 0.000633$ $\infty = 1.0930$

Temp.	v	f obs.	f calc.	Diff.
0	1.1600	104.3	105.9	1.6
25	1.1845	144.0	144.6	0.6
40	1.2097	185.3	184.3	—1.0
55	1.2367	226.0	227.0	1.0

ETHYL ALCOHOL-METHYL ACETATE $c = 0.000614$ $\infty = 1.0660$

Temp.	v	f obs.	f calc.	Diff.
0	1.1343	111.2	111.3	0.1
25	1.1676	163.2	165.2	2.0
40	1.1912	202.1	203.8	1.7
55	1.2140	241.4	240.9	—0.5

The above tabulated values are shown graphically in Fig. IV.

It will be seen that in all cases where the viscosity composition curve shows a maximum the fluidity volume curve is concave to the fluidity axis, and where the former is straight or nearly so the latter is also straight. One exception will be noticed, namely pyridine-aniline. Here the viscosity isotherm is nearly straight and the fluidity volume curve is decidedly curved. This may possibly be due to the fact that there is a compound formed but if so its viscosity is nearly the same as that calculated for the mixture from the mixture rule and therefore does not cause a maximum.

We consider these facts to be additional evidence of the existence of compounds in certain liquid mixtures and to support the theory that viscosity maxima are indicative of the presence of compounds. The converse, that the absence of a maximum indicates the absence of a compound, is not necessarily true.

We wish to express our gratitude to Miss E. McDaniel for valuable assistance in determining the viscosity isotherms for the mixtures, pyridine-ethyl acetate, ethyl alcohol-ethyl acetate, and ethyl alcohol-methyl acetate, which had not previously been worked out, and for determining the viscosities of the same mixtures at the different temperatures given.

The appended bibliography does not purport to be a complete list of the work on the subjects covered, but it includes the most important matter on viscosity of pure liquids as far as it applies to chemical and molecular constitution, and work on the physical properties of mixtures of completely

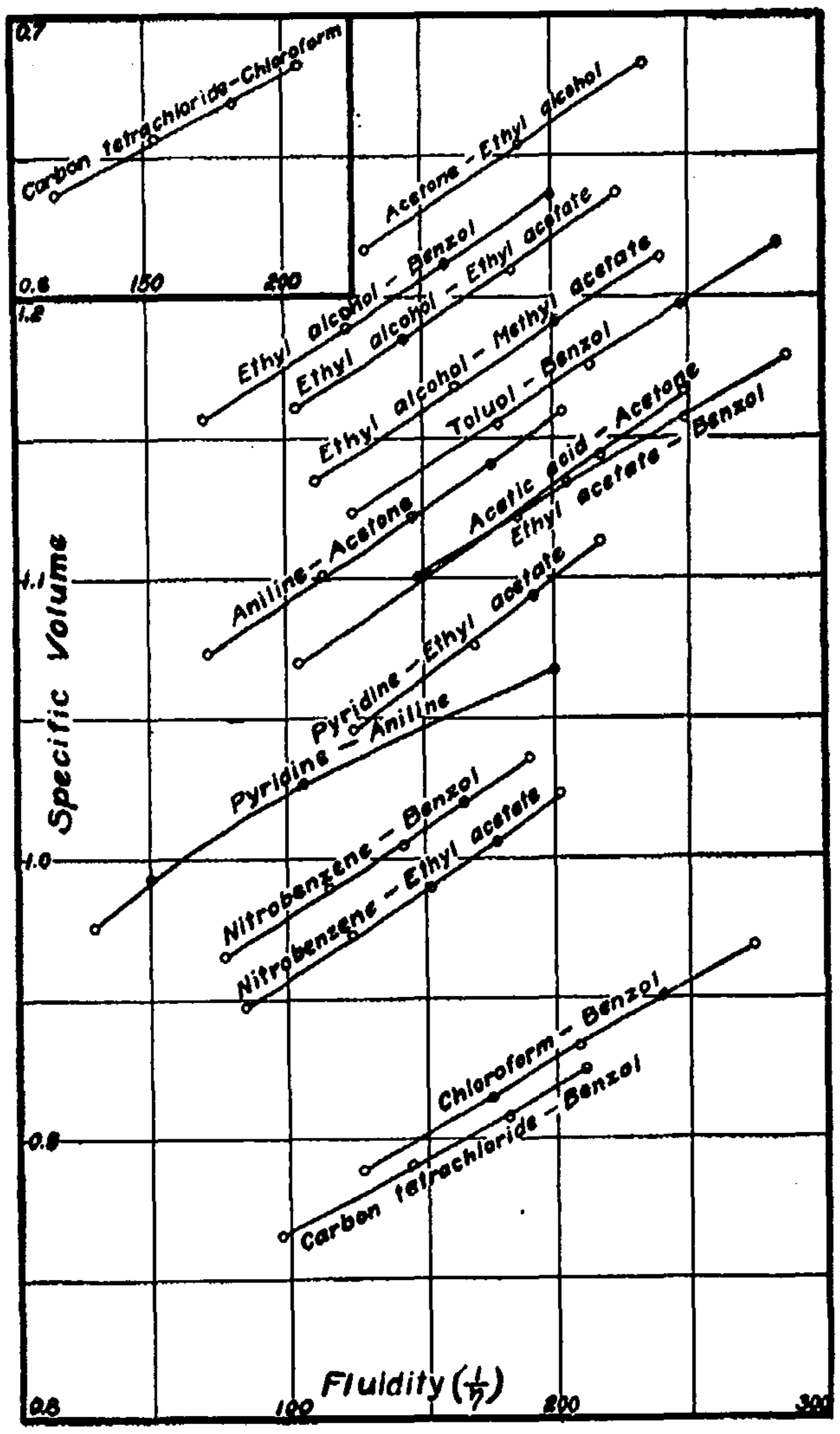
0.7
0.6
150
200
Carbon tetrachloride-Chloroform
Acetone - Ethyl alcohol
Ethyl alcohol - Benzol
Ethyl alcohol - Ethyl acetate
Ethyl alcohol - Methyl acetate
Toluol - Benzol
Acetic acid - Acetone
Ethyl acetate - Benzol
Aniline - Acetone
Pyridine - Ethyl acetate
Pyridine - Aniline
Nitrobenzene - Benzol
Nitrobenzene - Ethyl acetate
Chloroform - Benzol
Carbon tetrachloride - Benzol
1.2
1.1
1.0
0.8
Specific Volume
0.8
100
200
300
Fluidity $(\frac{1}{\eta})$

Fig. IV

miscible liquids which had been published up to January 1, 1914.

LITERATURE ON VISCOSITY OF PURE LIQUIDS AND ALL PROPERTIES OF LIQUID MIXTURES

R. D. Cooke

Viscosity of pure liquids	1 to 28
Viscosity of liquid mixtures	29 to 70
Surface tension of mixtures	71 to 81
Optical properties of mixtures	82 to 94
Thermal properties of mixtures	95 to 108
Densities of mixtures	109 to 119
Miscellaneous properties	120 to 148
Theory of mixtures	149 to 169
Boiling point and vapor pressure	170 to 221

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Laboratory of Physical Chemistry
University of Wisconsin
Madison, Wisconsin
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THE COPPER LAKES OF EOSIN

BY HARVEY NICHOLAS GILBERT

In view of the colloidal nature of the lakes formed by the metallic bases with the dye eosin, and the peculiar behavior of these lakes under certain conditions, the study of a typical eosin lake was undertaken in order to determine whether the lake was a definite compound or merely an adsorption complex, consisting of the metallic base with the eosin adsorbed in approximately equivalent amount.

The eosin lakes were first described by Baeyer in his research on the compounds of phthalic acid with the phenols.[1] With the exception of a brief reference to several of these lakes by Meyer,[2] no further work has been done with these compounds and the colloidal properties of the lakes have never been investigated. The lakes are composed of the base, or metallic hydroxide, and the acid eosin, both of which are colloidal. The bases carry positive charges when suspended in water and move to the cathode under the influence of the electric current. The acid, eosin, which is insoluble in water and usually is obtained as a gelatinous solid, carries negative charges and moves to the anode under the influence of the current. In view of the known cases of precipitation of a colloid carrying a positive charge, by a negatively charged colloid in more or less definite proportions, it seemed possible that these lakes, which were always produced by adding equivalent amounts of the metallic salts to the alkali salts of eosin, might be colloidal complexes of this nature.

The lakes of silver, lead, copper, zinc, aluminum, cobalt, iron, both ferric and ferrous, manganese and bismuth, were obtained as amorphous substances which gave analyses corresponding in general to the normal salt of the dibasic acid, eosin. In other cases, the amorphous lake thus produced,

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[1] Liebig's Ann., 183, 43 (1876).

[2] Ber. chem. Ges., Berlin, 29, 2625 (1896).

changed over into definite crystalline compounds upon standing for various lengths of time, and these crystalline compounds gave analyses corresponding to the normal salts of eosin. There could be no doubt concerning the composition and nature of these crystalline salts of calcium, barium, cadmium, nickel, and mercury (divalent).

The copper lake was selected as typical of the class of colloidal substances. Baeyer obtained it by precipitating a copper sulphate or copper acetate solution, by means of sodium eosinate, and he described it as an amorphous, red-brown precipitate. The formula for the normal salt, $CuC_{20}H_6Br_4O_6$, was assigned to it. In some preliminary experiments with this lake when treated with ether, it was found that some eosin was removed from the lake by the ether. Other experiments on the effect of the addition of alcohol or acetone to the lake, gave a light yellow solution and a subsequent separation of a light blue solid, presumably copper hydroxide. It was with a view to the explanation of these phenomena, together with a study of the composition and properties of the lake that this work was undertaken.

Material and Methods of Analysis

The eosin used was obtained from Merck as "eosin yellowish," described as the alkali salt of tetra-brom fluorescein. Analysis showed it to be the sodium salt of this acid. However, all analyses were made on the basis of the (acid) eosin content, and all statements of concentrations are referred to this value. It must be borne in mind that the free acid, eosin, is practically insoluble in water but soluble in ether, while the alkali salts of eosin are soluble in water but insoluble in ether.

In order to facilitate the work of analysis, a colorimetric method was devised. This was possible because of the high coloring power of the eosin radical which thus permits the use of very dilute solutions. A source of error to be avoided was the change of color when reflected light strikes a solution of eosin, due to the fluorescence produced. This was rendered negligible by using the Wolff colorimeter, in which the column of solution is protected from the source of light. It was impossible to use electric light, from either the carbon or tungsten lamps, as the color of the solutions under these lights became a yellowish tint, very difficult to distinguish. The question of end-point was very important because of the marked change in color of the solution upon dilution. Sodium eosinate in concentrated solution is a dark blood-red color which on dilution goes through various shades of yellowish red which are very hard to follow or to differentiate. However, when the solution becomes very dilute, this color change with increased dilution is very marked and was found to be most delicate when the concentration of eosin (acid) is 0.00125 gram per liter. At this concentration, the solution is a fine light pink which is rapidly shaded into an old rose with stronger solutions, and an equally rapid fading of color is observed on dilution. A solution of this strength was, therefore, chosen as the standard, and all determinations were made by diluting the unknown solution to this strength, in the usual manner.

In order to avoid the fading of color due to the action of light—which is one of the greatest failings of the dye eosin —a solution of $Co(NO_3)_2$ was employed in place of this standard solution, as it was found that a solution containing 17.84 grams of $Co(NO_3)_2$ per liter, had exactly the same color as the standard, and was permanent to light. Accordingly, 100 cc of this standard were placed in the one cylinder and the unknown solution was diluted until the color just matched that of the standard. In order to standardize the cobalt nitrate solution, a weighed amount of free eosin acid was treated with ammonium hydroxide and diluted until the color was that of the standard cobalt nitrate solution, and from this, the amount of eosin producing the color of the standard solution was determined. The standard eosin (acid) may be obtained from an aqueous solution of the alkali salt by adding a slight excess of any strong acid and shaking with ether in a separatory funnel. The ether removes the eosin completely. This ether solution is then evaporated and dried at 100° in a tared flask. The residue consists of free eosin and is weighed as such. Sulphuric acid was used throughout this investigation to bring about the decomposition of the eosin compounds. An example of this is given:

Sodium eosinate solution Cc	Weight of eosin Gram	Eosin per cc. Gram
9.88	0.0408	0.00413
14.93	0.0627	0.00420

In another experiment 10 cc of sodium eosinate solution were found to contain 0.0103 gram per cc when determined by this gravimetric method, while 10 cc of the same solution when analyzed by the colorimetric method, gave 0.0104 gram per cc. This shows a good agreement between the two methods. An alcoholic solution of sodium eosinate when diluted directly with water, was found to contain, in duplicate determination, concentrations of 0.004965 and 0.004960 gram of eosin per cc.

In the experimental work which follows, the errors due to other conditions of the experiments were usually much larger than the limits of accuracy of the method of analysis. Checks were made from time to time throughout the work and the agreement between the gravimetric and colorimetric method was entirely satisfactory. The color is in the eosin acid radical and it makes no difference whether the solution which is to be diluted contains the eosin as the sodium or the ammonium salt, although the latter was usually employed for convenience.

The determination of eosin in any of its compounds with the metals may be made by decomposing the aqueous solution by means of an excess of acid, sulphuric or nitric, in the presence of ether. The eosin goes into the ether layer and may be then determined colorimetrically as just described. The other salts used in this work were C. P. and were obtained from Merck. The ether was obtained from Kahlbaum and contained no traces of acid.

Study of the Behavior of Eosin in Ether Solution toward Copper Hydroxide

It is difficult to obtain copper hydroxide free from water when it is prepared by precipitation from aqueous solutions. In order to avoid this difficulty the precipitation was made from alcoholic solutions of copper nitrate and sodium hydroxide. The copper hydroxide was washed by decantation, first with alcohol, to remove the $NaNO_3$ which was formed by the reaction, and afterwards with ether, which is readily miscible with alcohol. This $Cu(OH)_2$ suspension in ether was then treated with ether solutions of eosin (acid), in which the amount of eosin in constant volume of solution was varied. In each case, the amount of $Cu(OH)_2$ was equivalent to 0.0278 gram of copper and the ether solution of eosin of known strength was added to this suspension, contained in a 250 cc glass-stoppered Erlenmeyer flask. The mixture was diluted to 150 cc and shaken from time to time. After two days the supernatant liquid was found to contain no traces of copper, and the solutions were analyzed colorimetrically for eosin. The solid remaining in the flasks varied in color from a light pink to a scarlet as the concentration of the eosin increased. The results are shown in Table I.

TABLE I

Standard eosin solution contained 0.0056 gram per cc
Theoretical weight of eosin for $Cu(OH)_2$ = 0.2786 gram

Cc of standard eosin solution diluted to 150 cc	Total eosin in original solution Grams	Total eosin in supernatant ether solution Grams	Eosin taken up by solid Grams
1	0.0056	None	0.0056
5	0.0279	0.0057	0.0222
10	0.0557	0.0342	0.0215
15	0.0835	0.0558	0.0277
20	0.1114	0.0840	0.0274
25	0.1393	0.1062	0.0331
50	0.2786	0.2502	0.0284

Thus it is seen that although equivalent amounts of

$Cu(OH)_2$ and eosin were brought together, approximately $^1/_{10}$ of the theoretical amount was taken up by the $Cu(OH)_2$.

To show the influence of increase of temperature on this equilibrium, equivalent amounts of $Cu(OH)_2$ and eosin as above, in 150 cc were heated on a water bath for four hours, the ether being retained by using a reflux condenser. The ether solution was then analyzed for eosin.

Eosin in original solution Gram	Eosin in resulting solution Gram	Eosin in solid Gram	Increase Gram
0.2786	0.2502	0.0284	—
0.2786	0.2429	0.0358	0.0074

From this it is seen that there is very little increase on boiling the $Cu(OH)_2$ with ether solution containing an equivalent amount of eosin, and that the maximum amount taken up in these operations is less than one-fifth of the theoretical. The curve (Fig. 1) plotted from the values given in Table I, gives the typical form for adsorption, although the experimental error is large. Hence there is no good evidence of the formation of a definite compound, copper eosinate, under these conditions, although the first portion of the curve might indicate the formation of a compound, which covered the surface of the $Cu(OH)_2$ and was insoluble in ether.

In order to ascertain whether the eosin removed from the solution by the $Cu(OH)_2$ was adsorbed on the surface, as the curve seemed to indicate, or whether it was chemically combined to form a coating of compound over the surface, which then prevented further action, experiments were made on the reversibility of this adsorption. The lake is insoluble in ether as is shown in these experiments by the absence of copper in the resulting solution. A portion of the lake was then prepared as described, by treating the $Cu(OH)_2$ with eosin in ether solution. The amount of eosin taken up was a definite amount and gave a point on the upper portion of the curve.

Eosin in original solution Gram	Eosin in resulting solution Gram	Eosin taken up Gram
0.2280	0.1960	0.0320

The supernatant ether solution was then removed by decantation and the amount remaining in the mother liquor was estimated to be 0.0196 gram since the original volume was 150 cc and 135 cc were decanted. The suspension was then diluted with 135 cc pure ether and after shaking, allowed to settle. On analysis, the supernatant liquid was found to contain 0.0210 gram eosin, showing that 0.0014 gram eosin had been removed from the lake. This should theoretically have given a point which was on the curve.

When these values are plotted, however, the point is found to be above the curve obtained for the adsorption, showing that the lake does not give up as much eosin as is required for the reversal of the curve. However, it is probable

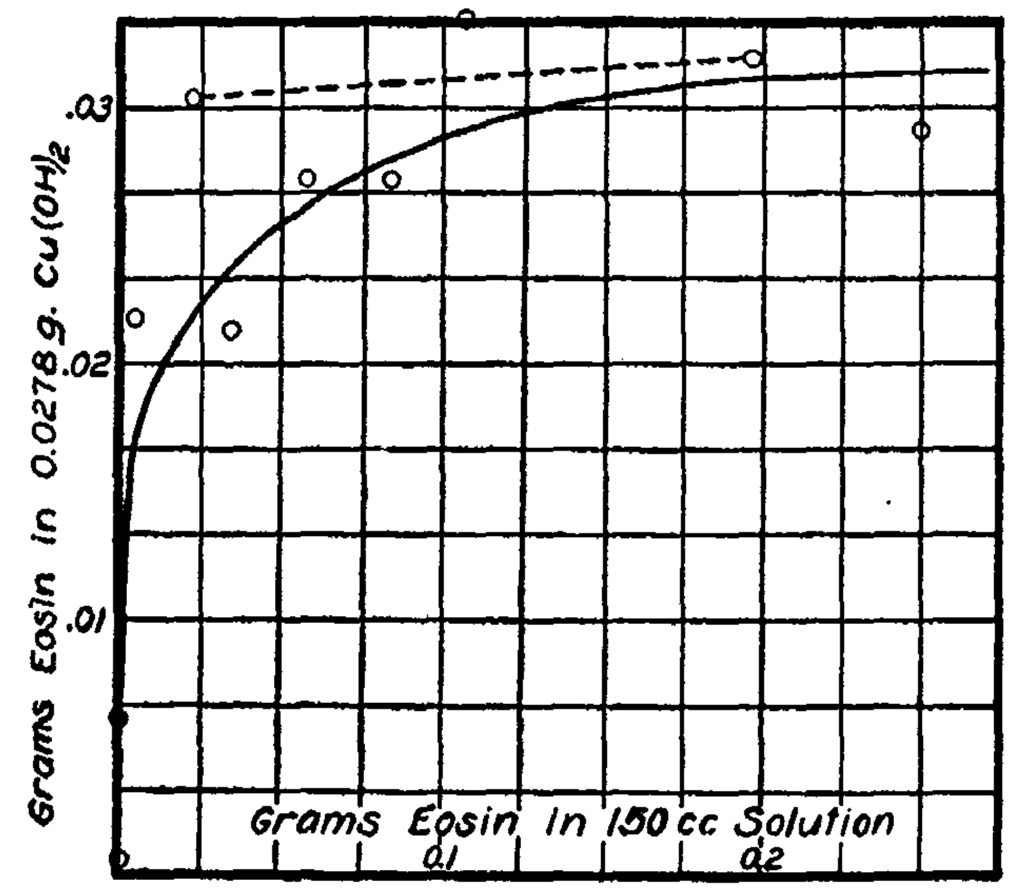

Fig. 1

that the $Cu(OH)_2$ had undergone a change in its physical condition on standing over this length of time, and an agglomeration of the lake would account for this retention of the eosin.

An analogous case was studied using magnesium oxide and eosin in ether solution. In these experiments, 0.07 gram MgO was weighed out and placed in a 250 cc glass-stoppered Erlenmeyer flask and to this was added the solution of eosin in ether. The volume of the solution was 200 cc in each case and the eosin content was varied. The flasks were shaken from time to time and allowed to stand several days at room temperature. The supernatant liquid was then decanted and analyzed for eosin by the colorimetric method. It was found that the ether solution contained no Mg, so that the change in concentration represented the amount of eosin taken up by the MgO. The results are shown in Table II.

TABLE II

Theoretical weight of eosin for compound = 1.134 grams

Eosin in original solution Gram	Eosin in supernatant solution Gram	Eosin taken up by solid Gram
0.0046	0.0029	0.0017
0.0230	0.0066	0.0164
0.0460	0.0180	0.0280
0.1150	0.0448	0.0702
0.2300	0.1180	0.1120
0.3450	0.1850	0.1600
0.4600	0.2370	0.2230
0.9200	0.6080	0.3120

When the values for eosin in the resulting solution are plotted as abscissas and the amount of eosin taken up by the solid, as ordinates, the following curve, Fig. 2, is obtained. This is the usual form for adsorption and shows that the MgO takes up a continuously varying amount of eosin depending on the original concentration, and on that of the eosin in the MgO.

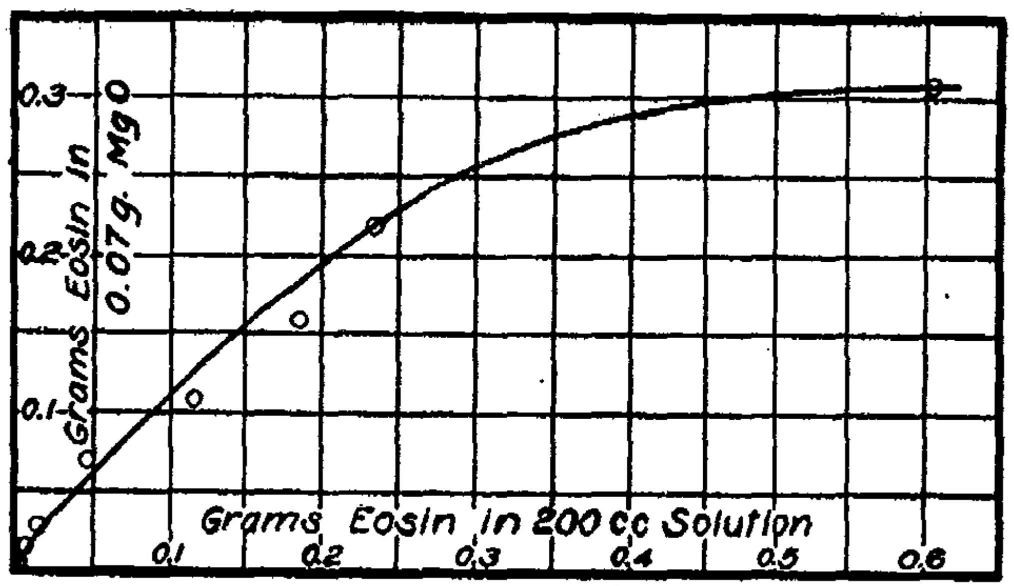

Fig. 2

Composition of Lake

When an aqueous solution of $CuSO_4$ is mixed with an aqueous solution of sodium eosinate, ordinarily, a red-brown gelatinous precipitate is formed. This precipitate produced by adding equivalent amounts of $CuSO_4$ and sodium eosinate had previously been analyzed and was found to contain copper and eosin in equivalent proportions. The formula for copper eosinate, $CuC_{20}H_6Br_4O_5$, was, therefore, assigned to it. Inasmuch as the precipitate so produced, had been obtained by mixing equivalent amounts of the two constituents, it was decided to vary these proportions and to study the precipitate formed when the concentrations were varied.

The following series of experiments were made by adding to 50 cc of a standard solution of $CuSO_4$, a constant volume of sodium eosinate solution in which the concentration of the sodium eosinate was varied over wide limits. After allowing to stand for twenty-four hours, the solutions were decanted and this decanted liquid was run through a small filter, the first 50 cc of the filtrate being rejected in each case. The filtrate was then analyzed for eosin colorimetrically and for copper by the electrolytic method. A summary of these results is found in Table III.

TABLE III

Original solution contained 0.0842 gram copper in each experiment

	Eosin in original solution Grams	Eosin in resulting solution Gram	Eosin in precipitate Gram
1	0.0520	0.0022	0.0498
2	0.0954	0.0021	0.0933
3	0.1901	0.0019	0.1882
4	0.2778	0.0011	0.2767
5	0.3730	0.0033	0.3697
6	0.5200	0.0024	0.5176
7	0.6930	0.0018	0.6912
8	0.8670	0.0029	0.8641
9	1.3500	The solutions were jelly-like and would not settle	
10	1.8000		

	Copper in resulting solution Gram	Copper in precipitate Gram	Theoretical Cu for eosin in precipitate Gram
1	0.0532	0.0310	0.0049
2	0.0042	0.0800	0.0092
3	0.0630	0.0212	0.0185
4	0.0462	0.0380	0.0272
5	—	—	0.0362
6	—	—	0.0508
7	0.0266	0.0576	0.0678
8	0.0126	0.0716	0.0820

These results are only approximate, and have a large experimental error, due to the colloidal nature of the lake which is formed. However, they show that the copper and eosin tend to be precipitated in equivalent amount, as was found by Baeyer. The excess of the copper in the precipitate which is formed when a large excess of copper salt was present, is to be noted, and will be explained by results obtained in experiments described later.

Properties of the Lake

This lake has many remarkable properties which mark it as colloidal. Depending upon the conditions under which it is prepared, it may remain in suspension and not precipitate at all, or it may form as a gelatinous precipitate. It is even possible to obtain it as a jelly. Thus, when the lake is formed from $CuSO_4$ and sodium eosinate by adding 50 cc $CuSO_4$ solution, containing 0.0820 gram copper, to 250 cc. of a sodium eosinate solution containing 0.8670 gram eosin (equivalent amount), a precipitate is obtained, and the supernatant solution contains an amount of the lake corresponding to 0.0029 gram eosin in 300 cc, or 0.0000097 gram per cc. When approximately 1.5 or 2 equivalents of sodium eosinate are added under similar conditions, the precipitate remains permanently suspended and cannot be cleared even by means of a centrifuge.

If to 25 cc sodium eosinate, containing 0.2008 gram eosin, are added an equivalent amount of copper sulphate solution, a precipitate is obtained, and this suspension, when diluted with 175 cc of water, gives a clear red solution. This solution contains 0.00103 gram eosin per cc.

When 10 cc of sodium eosinate solution, containing 0.0428 gram eosin, were added to 1.31 cc of copper sulphate solution containing an equivalent amount of copper, a precipitate is formed. This suspension when diluted with 50 cc of water gives a hazy, brownish red solution containing no visible solid matter. This material passed through the filter although the filtrate was still hazy. On the further addition of 40 cc of water, a fine, clear red solution resulted, and this contained the equivalent of 0.00428 gram eosin per cc.

When 25 cc sodium eosinate solution containing 0.1540 gram eosin, are mixed with 4.71 cc $CuSO_4$ solution containing an equivalent amount of copper, a precipitate is formed which requires dilution to approximately 250 cc before a clear solution is obtained. This solution remains fairly clear for one week, and contains 0.000616 gram eosin per cc.

Hence this lake has a variable apparent solubility which is difficult to determine accurately because of the colloidal nature of the substance and because of the method of formation. The apparent solubility ranges from about 0.00001 gram of eosin per cc for the solution in contact with the solid, to 0.0005 gram eosin when the lake is diluted by adding water.

This lake may also be obtained in the form of a jelly. Thus when 10 cc of a solution of sodium eosinate, containing 0.02748 gram eosin per cc are treated with the equivalent amount (0.956 cc) of a 0.4432 *N* $CuSO_4$ solution, a red-brown precipitate is formed which is suspended in the water and is not unusually viscous. After standing 30 seconds, the suspension begins to darken. In 60 seconds the mass is very viscous and in two minutes a jelly-like structure is formed which remains in an inverted beaker. Likewise, a jelly is formed almost immediately when 2.32 cc $CuSO_4$ (0.4432 *N*) is added to 10 cc of a solution of sodium eosinate containing 0.0666 gram eosin per cc.

The lake does not diffuse through parchment although when suspensions of equivalent amounts of $CuSO_4$ and sodium eosinate are placed in the *Hülsen* parchment thimbles and dialyzed for several days with water, a slight pink color is found in the water. This never amounts to more than 0.000000125 gram eosin per cc and is probably due to a small amount of Na eosinate which is present, as will be explained later. The concentration of this amount which diffused through was so small that no tests could be made for copper, but it is most probably sodium eosinate. Similar tests with sodium eosinate, which is a definite crystalline compound, gave a rapid diffusion through the parchment.

The solution of the lake in water is not much affected by salt solutions. NaCl and $NaNO_3$ have little effect on it. A solution of Na_2SO_4 tends to produce a precipitate of copper hydroxide on long standing. Solutions of $Cu(NO_3)_2$ and $CuSO_4$ produce a precipitate from the aqueous suspensions of the lake and this precipitate is found to be a mixture of $Cu(OH)_2$ and eosin (acid). This may be shown by shaking the suspension with ether. The greater part of the precipitate is dissolved in the ether, thus showing that a large portion of the precipitate consisted of eosin. The remainder of the original precipitate was colored light blue and remained suspended in the water layer. However, this behavior with salts and the aqueous solution of the lake is not easy to study because of the low concentrations, and it will be taken up in another form under a different method of treatment.

Synthesis of the Lake

It was then attempted to synthesize the lake directly from the constituents in water suspension, that is, from eosin (acid) and $Cu(OH)_2$. Copper hydroxide is prepared from copper salts by the addition of NaOH, and this precipitate is washed by decantation several times. Thus prepared, it is an amorphous, colloidal precipitate, insoluble in water.

Eosin was prepared from sodium eosinate by adding a strong acid, decanting the supernatant liquid and washing the precipitate by decantation. As thus prepared, it is an amorphous colloidal precipitate, giving a colloidal suspension in pure distilled water. Eosin is completely insoluble in water containing slight traces of acid.

The following experiments were performed by mixing suspensions of these two constituents in varying proportions as specified, and observing the properties of the resulting solutions. The standard suspension of eosin was obtained by adding an excess of H_2SO_4 to 308 cc of sodium eosinate, containing 0.01056 gram eosin per cc. The eosin (acid) thus precipitated, was washed by decantation and diluted to 700 cc. The suspension of $Cu(OH)_2$ was prepared by adding a slight excess of NaOH to 20 cc $CuSO_4$ solution containing 0.0399 gram copper per cc. This precipitate was also washed by decantation and the suspension was diluted to 700 cc.

These suspensions were of such concentration that equal volumes contained equivalent amounts of copper and eosin.

No. 1

50 cc eosin suspension.
50 cc $Cu(OH)_2$ suspension + 200 cc H_2O
Equivalent to 1 molecule of eosin and 1 molecule $Cu(OH)_2$.

A thick suspension was formed and no change was observed in two days. On the third day crystals formed on the bottom of the beaker and the solution had become clear but red-brown. The residue under the microscope was uniformly crystalline, consisting of needle crystals.

No. 2

50 cc eosin suspension.

100 cc $Cu(OH)_2$ + 150 cc H_2O.

Equivalent to 1 molecule eosin and 2 molecules of $Cu(OH)_2$.

A thick suspension resulted, and after three days a few crystals had formed in places on the sides of the beaker; after thirteen days more crystals had formed. Under the microscope the residue was found to consist of much amorphous matter mixed with a few crystals.

No. 3

50 cc eosin suspension.

25 cc $Cu(OH)_2$ + 225 H_2O.

Equivalent to 2 molecules of eosin and 1 molecule of $Cu(OH)_2$.

No crystals formed in twenty days. There resulted an orange colored suspension, while a red amorphous mass settled in the bottom of the beaker. This residue showed no crystals under the microscope.

To show the effect of dilution on the rate of transformation:

No. 4

25 cc eosin suspension.

25 cc $Cu(OH)_2$ + 400 cc H_2O.

The suspension was almost clear and no residue settled to the bottom. No crystals were formed until 21 days, when fine long needle crystals were obtained.

No. 5

25 cc eosin suspension.

50 cc $Cu(OH)_2$ suspension + 400 cc H_2O.

This gave some amorphous sediment in 24 hours. No change from this was apparent until about 21 days when some crystals were found by examination of the residue from the bottom of the beaker; under the microscope this was found to be mixed with much amorphous matter.

In order to determine the solubility of the lake prepared by adding equivalent amounts of $Cu(OH)_2$ and eosin, 308 cc sodium eosinate (0.0324 *N*) were converted into eosin (acid) by adding an excess of H_2SO_4 and washing by decantation. The $Cu(OH)_2$ was prepared by precipitation from 20 cc of $CuSO_4$ solution (0.500 *N*) by means of KOH, with subsequent washing by means of decantation. These suspensions were each diluted to 1500 cc and mixed. A red-brown cloudy suspension was obtained which did not change in 48 hours. This suspension passed through the filter paper. When 200 cc of the cloudy suspension were diluted to 500 cc a clear solution was obtained which contained the equivalent of 0.000213 gram eosin per cc. Hence the solubility is of the same order as that of the lake prepared by double decomposition.

When the above amounts of sodium eosinate and $CuSO_4$ (equivalents) are each diluted to 500 cc and the solutions are mixed, there results an amorphous precipitate resembling the synthesized material and this suspension on standing fifteen days deposited crystals of the same needle form, which were identical with the crystals formed by direct synthesis.

All these synthetic lakes, upon dialysis with parchment paper, gave only a small amount of colored material to the water outside of the parchment cup, and this small amount was probably due to sodium eosinate which was formed, as will be explained later. It may have been due, however, to the crystalline copper eosinate, since the amount was not greater than the solubility of crystalline copper eosinate in water.

When the lake is freshly prepared by adding the suspensions of eosin and $Cu(OH)_2$ in varying proportions, and immediately diluting with water, hazy solutions are obtained which may be passed through the filter paper without leaving any residue. These results were obtained by using the $Cu(OH)_2$ and eosin suspensions just described, in the amounts stated in Experiments 1, 2, and 3. Nos. 1 and 2 were diluted with 400 cc of water, while No. 3 required dilution to 600 cc.

All of these suspensions containing varying amounts of copper hydroxide and eosin might be called definite compounds with as much justification as the lake produced by copper sulphate and sodium eosinate because, disregarding the effect of adsorption, the latter must necessarily contain eosin and $Cu(OH)_2$ in equivalent proportions, no matter what concentration of $CuSO_4$ or sodium eosinate was employed. This is better understood when it is considered that when $CuSO_4$ and sodium eosinate are mixed, if the precipitate contains other than equivalent amounts of copper on eosin the resulting solution must become either acid or alkaline, and either of these conditions would destroy the lake. Thus, if an excess of sodium eosinate were used, and more than an equivalent amount of eosin were taken up by the lake, NaOH would be set free. Likewise, if an excess of $CuSO_4$ were used, and more than an equivalent amount of Cu were taken up by the lake, an excess of H_2SO_4 would result. The lake of course is instable in the presence of either of these, since copper hydroxide is a much weaker base than sodium hydroxide and sulphuric acid is much stronger than eosin acid. In the case of these synthetic lakes, therefore, the same behavior is observed as in the case of the lake containing equivalent amounts of the constituents, and the composition of these lakes may be made to vary at will.

The rate of transformation from the amorphous to the crystalline is hastened by the presence of some copper eosinate crystals ("seeded in") . Thus 110 cc eosin suspension and 110 cc $Cu(OH)_2$ suspension, on the addition of a few crystals, gave crystals in two days and a large amount had deposited in three days. The clear, red-brown, supernatant liquid was decanted and allowed to stand 13 days, at which time many crystals had deposited from it.

Some crystals were prepared by adding 100 cc eosin suspension to 100 cc $Cu(OH)_2$ suspension and allowing the mixture to stand 23 days. The residue consisted of a uniform mass of crystals. These crystals were dried, analyzed, and found to contain eosin and copper in the proportion of 1 atom of copper to 1 molecule of eosin, and, therefore, consist of the normal salt of the acid eosin, the formula for which is $CuC_{20}H_6Br_4O_5$.

The transformation of the colloidal copper lake into the crystalline form was thus observed for the first time. Similar phenomena had been observed by Baeyer[1] in the case of the cadmium lake, which changed over into the crystalline form in about eight hours, and in the cases of the nickel, barium, calcium, and mercuric compounds.

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[1] Liebig's Ann., 183, 43 (1876).

Colloidal sulphur on standing goes over to the crystalline form.[1]

Recently, a similar phenomenon was observed in the change of mercuric sulphide from the colloidal to the crystalline form.[2]

Properties of the Crystalline Copper Eosinate

Crystalline copper eosinate is practically insoluble in water, acetone or alcohol. In no case does the solubility amount to more than 0.000004 gram eosin per cc. However, for some unknown reason, it is more soluble in a mixture of equal parts of acetone and water, and in a mixture of equal parts of alcohol and water than in the pure solvents. Relatively large excess of Cu salts or of other salts have no effect on the crystalline copper eosinate. It is difficult to decompose with acids. When placed in water and shaken with ether, it goes entirely into the surface between the two layers, giving a film which resembles the purple skin of a grape, by reason of the steel blue color of the crystal product itself. The crystals are monoclinic.

The crystalline material, when ground in a mortar under water does not show any increase in solubility, as would be expected if the lake is composed of an amorphous copper eosinate, since these conditions are more nearly approached by grinding the crystalline material.

Behavior of the Lake with Ether

When the copper-eosin lake is prepared by bringing together equivalent amounts of sodium eosinate and copper salts in aqueous solution and this suspension of the lake is shaken with ether, considerable amounts of eosin are found to be taken up by the ether. Thus, 40 cc sodium eosinate solution containing 0.1668 gram eosin were added to 19.87 cc $Cu(NO_3)_2$ solution, containing 0.0167 gram Cu, and the lake was diluted with 15 cc water. 100 cc ether were added and the mixture was shaken for one hour on a shaking machine. The ether solution was found to contain 0.0428 gram of eosin.

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[1] Raffo: Zeit. Kolloidchemie, **2**, 358 (1908).

[2] Freundlich and Schucht: Zeit. phys. Chem., **85**, 660 (1913).

A duplicate experiment in which the mixture was shaken for five hours, removed 0.04284 gram eosin. When this experiment was repeated, using the same amounts of sodium eosinate and an excess of copper nitrate corresponding to 15 cc of $N/5$ $Cu(NO_3)_2$, the ether was found to remove 0.0585 gram of eosin.

Similar results were obtained by treating the lake prepared from $CuSO_4$ solution with ether. Thus, when 4.71 cc $CuSO_4$ solution (0.0505 N) are added dropwise to 95 cc of a sodium eosinate solution containing 25 cc (0.0095 N) sodium eosinate and the suspension is shaken with 100 cc. of ether, 0.0200 gram of eosin is removed by the ether. It was also observed that when this experiment was repeated, by adding the same amount (equivalent) of $CuSO_4$, diluted to 50 cc, to the sodium eosinate solution diluted to 50 cc, less eosin was removed by the ether. In this case the ether contained 0.0180 gram eosin. From these preliminary experiments it was found that eosin could be removed from the lake in aqueous suspension by shaking with ether. This amount depends upon the conditions under which the lake is prepared, and upon the nature of the original copper salt employed. It is also seen that equilibrium is obtained comparatively rapidly.

An experiment was then performed to ascertain whether more eosin was removed by fresh ether after this first equilibrium had been obtained. Equivalent amounts of $CuSO_4$ and sodium eosinate as described in the preceding experiment, were diluted to 50 cc and mixed. The lake was shaken with ether and as in the preceding experiment, it was found that 0.0185 gram eosin was removed. This ether solution was removed by pipetting off as much as possible and the volume was noted. A volume of fresh ether equal to the volume removed was then added to the lake and the suspension was again shaken. The eosin in the ether layer was estimated and it was found to be practically the same as the amount left in the solution which could not be pipetted off. A slight increase of 0.0005 gram eosin may have been due to experimental error. It is quite evident, therefore, that we are not dealing with a reversal of the adsorption of eosin by the lake, for if such were the case, the amount removed by the fresh ether would probably have been appreciable, although less than that obtained by the first washing.

It was then decided to investigate this removal of eosin by means of ether, more thoroughly. In the following experiments, the lake was prepared by precipitation under the conditions specified in each case. The precipitation was carried on in 250 cc glass-stoppered Erlenmeyer flasks and these were placed, two at a time, in an ordinary milk-shaking machine and shaken for the specified time. It was found that equilibrium was ordinarily reached before one-half hour had elapsed. It was found necessary to work with small concentrations because when stronger concentrations were employed, the ether and water formed an emulsion which was very difficult to break down. After shaking, the flasks were removed and allowed to stand several hours, in order to allow the lake to settle. It is interesting to note, although it does not lie within the province of this research, that in a great many cases, the lake was found to have gone almost completely into the ether layer, leaving a slightly colored, clear solution in the water layer. After the lake had settled, a portion of the ether layer was pipetted off and this solution was analyzed for eosin by the colorimetric method. This removal of the eosin by the ether was at first thought to be due to acid in the ether, although redistilled ether, which gave no tests for acid with litmus or methyl orange when tested in the prescribed way, was also found to cause the removal of the eosin. Experiments were then made, using other liquids which dissolve the acid, eosin, and which give a two liquid layer system with water. 25 cc of sodium eosinate (0.0095 *N*) were diluted to 50 cc and mixed with 4.71 cc of 0.0505 *N* $CuSO_4$ solution diluted to 50 cc. The resulting suspension of the lake was shaken for an hour with 100 cc of chloroform. A dark red emulsion resulted and this did not break down for several hours. The chloroform layer then contained 0.0123 gram of eosin.

When this same amount of the lake was shaken with 100 cc of benzene, an old-rose colored emulsion was obtained, which broke down partially after standing one day. The benzene layer was found to contain 0.0089 gram of eosin.

When this experiment was repeated, using 100 cc of CS_2 as the second liquid layer, a light pink emulsion was formed. This emulsion was rather viscous and it did not break down appreciably until it had stood for two days. The CS_2 was found to have removed 0.0048 gram of eosin from the lake. This difference in the total amount of eosin removed by the solvent may have been due to the different degrees of contact of the lake with the solvent. However, it shows that the removal of eosin from the lake can be accomplished by the use of solvents other than ether.

The sodium eosinate solution was then mixed with the ether to see if any eosin was removed. Ten cc of sodium eosinate (0.0095 *N*) were diluted to 100 cc and shaken with 100 cc of ether. The ether layer was found to contain 0.0031 gram of eosin. When 10 cc. of the sodium eosinate solution were diluted to 100 cc using freshly boiled distilled water, and shaken with 100 cc of ether, only 0.0016 gram of eosin was removed by the ether. This slight amount removed with pure distilled water was probably due to impurities in the original material—it is negligible in this work as it is below the experimental error.

From the preliminary experiments it was seen that an excess of copper salt increased the amount of decomposition of the lake, and the following experiments were performed to study further the effect of copper salt on this decomposition.

The following results were obtained by varying the amount of $CuSO_4$. In each experiment the $CuSO_4$ and the sodium eosinate were each diluted to 50 cc and 100 cc ether was shaken with the mixture.

TABLE IV

Sodium eosinate solution 0.0095 N
$CuSO_4$ solution 0.0505 N
Volume of aqueous suspension = 100 cc
25 cc eosin in each experiment

Cc. of $CuSO_4$	Molecular ratio Copper: Eosin	Eosin removed Gram	Total eosin present Gram
4.71	1	0.0190	0.0769
7.07	1.5	0.0294	0.0769
9.42	2	0.0480	0.0769
10.60	2.25	0.0657	0.0769
11.78	2.5	0.0735	0.0769
14.13	3	0.0760	0.0769

From these results, it is seen that almost complete decomposition is obtained at this dilution by an *excess* of 1.5 molecules $CuSO_4$.

But, at different concentrations of the lake, different amounts of decomposition are observed. The following experiments were performed by adding the $CuSO_4$ solution directly to the sodium eosinate solution and shaking with 100 cc of ether. The $CuSO_4$ solution was 0.0505 N, and the sodium eosinate solution 0.0095 N. Thus the amount of the lake was the same as in the preceding experiments, although the volume of the suspension was only 30 cc in these experiments. The results are shown in Table V.

TABLE V

Sodium eosinate solution 0.0095 N
$CuSO_4$ solution 0.0505 N
25 cc eosin in each experiment

Cc of $CuSO_4$	Molecular ratio Copper : Eosin	Eosin removed Gram	Eosin from Table IV Gram	Total eosin Gram
4.71	1	0.0125	0.0190	0.0769
6.00	1.25	0.0446	0.0240*	0.0769
7.20	1.5	0.0625	0.0294	0.0769
8.25	1.75	0.0765	0.0380*	0.0769

The results given in the fourth column are from Table IV and the values marked by the asterisk were obtained by interpolation. These results show that the amount of decomposition increases with increasing concentration of the copper salts and that the total amount of copper salt necessary to produce the same amount of decomposition, depends on the concentration of the lake in the aqueous suspension. The same amount of lake was used in the experiments shown in Tables IV and V, the dilution of the lake being the only factor which was varied. In the more concentrated suspensions, an excess of three-fourths of a molecule of $CuSO_4$ produced complete decomposition of the lake, while an excess of one and one-half molecules of $CuSO_4$ was necessary to decompose the suspension when it was more dilute.

The following experiments shown in Table VI, were made to study the effect of an excess of copper nitrate. The lake contained 0.0770 gram of eosin in each experiment, which was the amount used in the preceding experiments.

TABLE VI

Total conc. of $Cu(NO_3)_2$ per 100 cc.	Eosin removed by ether Gram	Remarks
0.0223	0.0240	Blank, containing equivalent copper and and eosin + 2 mols. $NaNO_3$
0.0446	0.0298	1 mol. $Cu(NO_3)_2$ in excess
0.0669	0.0290	2 mol. $Cu(NO_3)_2$ in excess
0.0892	0.0284	3 mol. $Cu(NO_3)_2$ in excess

Thus the decomposition increases with an increase in the concentration of the copper salt, as with the $CuSO_4$, although in this case, a maximum in the decomposition is reached before all the lake is decomposed.

In all these experiments, it was difficult to understand the decomposition produced when exactly equivalent amounts of the copper salt and sodium were used, unless this decomposition was caused by the presence of the sodium salt of the acid, which was formed by the reaction. The following experiments shown in Table VII were performed to study the effect of Na_2SO_4 on the lake:

TABLE VII

The lake contained 0.0770 gram eosin and its equivalent of copper in 100 cc H_2O

Total grams of SO_4 ions present	Eosin removed by ether Gram	Remarks
0.011	0.0250	Blank, 1 equiv. SO_4
0.045	0.0440	Equivalent to 3 mols.SO_4 *excess*
0.079	0.0520	Equivalent to 6 mols.SO_4 *excess*
0.148	0.0520	Equivalent to 13 mols.SO_4 *excess*

In the last two experiments, the water layer was colored a deep red, probably due to sodium eosinate. The copper hydroxide was not colored and floated on the surface between the ether and the water layer. This decomposition therefore explains the eosin set free when equivalent amounts of sodium eosinate and Cu_2SO_4 are mixed.

The following experiments were made to study the action of H_2SO_4 on the lake, and to determine whether the SO_4 ion in H_2SO_4 had the same effect as in the case of Na_2SO_4. Two preliminary experiments were made with sodium eosinate and H_2SO_4.

No. 1

10 cc sodium eosinate solution (0.0095 *N*), were diluted to 100 cc and 1 cc H_2SO_4 (0.0372 *N*) was added. Upon shaking with 100 cc of ether and analyzing the ether layer for eosin, it was found that 0.0119 gram eosin had been set free from the sodium eosinate by the H_2SO_4. The calculated amount of eosin corresponding to this strength of H_2SO_4 is 0.0120 gram.

No. 2

10 cc of the sodium eosinate solution was treated as in the preceding experiment with 2 cc of H_2SO_4 (0.0372 *N*).

The amount of eosin set free was 0.0250 gram, and this corresponds exactly to the strength of H_2SO_4 used.

These experiments check the strength of the H_2SO_4 solution, and show that it decomposes the sodium eosinate solution quantitatively.

Experiments were then made with the copper lake and H_2SO_4 in varying amounts. The lake was prepared in each case by diluting 4.71 cc. $CuSO_4$ (0.0505 N) to 45 cc and adding 25 cc of sodium eosinate solution (0.0095 N) which had been diluted to 50 cc. The amount of H_2SO_4 (0.0372 N), specified in each case, was then added, and after adding H_2O to make the total volume of the suspension equal to 100 cc, the suspension was shaken with 100 cc of ether and the eosin estimated as before. Inasmuch as a small amount of eosin had been shown to be removed from sodium eosinate by ether (due to impurities) and since sodium eosinate was in excess, this amount was deducted from the results obtained, and the values given in Table VIII are the values thus corrected.

TABLE VIII

Cc H_2SO_4	Eosin removed	Eosin equivalent to H_2SO_4
1.00	0.0123	0.0120
2.00	0.0232	0.0240
3.00	0.0353	0.0360
5.00	0.0520	0.0600

These results show that the lake is decomposed quantitatively by the H_2SO_4, as is the case with sodium eosinate. The amount of decomposition, and the behavior in general, is different from the effect of the same amount of SO_4 ion since the decomposition in this case is proportional to the amount of SO_4 ions present. This quantitative decomposition does not necessarily argue for the existence of a definite compound of copper and eosin, since the lake would be expected to behave in this manner if it were an adsorption complex consisting of $Cu(OH)_2$ and eosin in equivalent amounts. Thus, in the latter case, H_2SO_4 would act upon the $Cu(OH)_2$, forming $CuSO_4$, and the eosin which had been adsorbed in equivalent amount would then be set free in the same proportion. The possibilities of the decomposition being due to hydrolysis of the excess salt, suggested itself, since the salts of weak bases with strong acids give an acid reaction, due to a difference in dissociation. However, one of the products of this hydrolysis of the copper salt would be $Cu(OH)_2$, and after the first portion of the copper hydroxide had been produced, in order that the decomposition of the lake should proceed to completion, it is necessary to postulate that the acid would decompose the copper lake in preference to reaching an equilibrium with $Cu(OH)_2$. This seems improbable. Another objection is found in the fact that this decomposition decreases with increasing dilution, that is, the decomposition is less when there is less copper salt present, while hydrolysis increases with increasing dilution. A third objection to this is found in the fact that an excess of Na_2SO_4 causes complete decomposition of the lake. This is impossible on the assumption of hydrolysis, for it may be shown by the following experiment that Na_2SO_4 is slightly hydrolyzed to give an *alkaline* reaction. If a Na_2SO_4 solution is treated with solid eosin (acid) which is practically insoluble in water, a marked increase in color is noted, showing that considerable eosin has gone into the water. This increase is due to the formation of sodium eosinate from NaOH and eosin. When the same experiment is performed with the normal solutions of NaCl, $NaNO_3$ and sodium acetate, practically no change is noted in the NaCl solution. The $NaNO_3$ is colored less than the Na_2SO_4 and the sodium acetate is colored a dark red. A far more simple and complete explanation for this phenomenon is offered on the basis of the assumption that the lake consists of eosin absorbed by $Cu(OH)_2$. When salts are present, the $Cu(OH)_2$ adsorbs the different ions in different amounts, depending on the nature of the anion, and when the attraction for the anion is greater than that between the $Cu(OH)_2$ and the eosin, the eosin is accordingly set free. In order to check this, experiments were made to determine whether the adsorption of other substances by $Cu(OH)_2$ would displace part of the eosin in proportion to the amount which these substances were adsorbed by $Cu(OH)_2$. It has been shown[1] that colloidal ($Cu(OH)_2$ when precipitated in 10 percent NaCl, upon standing, gave an alkaline solution containing 0.2772 percent NaOH, and that this was caused by the adsorption of the Cl ion by the $Cu(OH)_2$; leaving the Na ions in the solution. Similar results may be obtained with Na_2SO_4, etc. Analogous results were obtained, using KCl and other solutions of salts. In a series of experiments made by Tommasi[2] on the stability of $Cu(OH)_2$ with temperature, it was found that the blue copper hydroxide became black with slight increase of temperature, but that the addition of different salts caused a marked increase of stability of the blue hydroxide and the temperature at which blackening just begins was determined for a number of salts, among which the following are of interest:

TABLE IX

Substance	Concentration Percent	Temperature of blackening (dehydration)
H_2O	—	77°
Na_2SO_4	10	79°
KCl	10	71°
KBr	10	85°
$MnSO_4$	10	no dehydration even at 100°
Sugar	10	

If this effect is considered as a measure of the adsorption of the anion or of the molecule, one could conclude that Br is adsorbed more than Cl ion, and the adsorption of $MnSO_4$ and sugar ought to be very marked. The following experiments were then made to determine the effect of these substances upon the stability of the lake in the presence of ether:

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[1] Comptes rendus, **92**, 453 (1881).

[2] Bull. Soc. chim. Paris, [2] **37**, 197 (1882).

TABLE X

Suspension of lake = 0.077 gram eosin and equiv. Cu

Substance	Conc. of substance added	Eosin removed	Remarks
$CuCl_2$	0.0856 g Cl per 100 cc	0.0290	Blank (no excess $CuCl_2$)
$CuCl_2$	0.1968 g Cl per 100 cc	0.0313	2 mols. $CuCl_2$ excess
$CuBr_2$	0.1880 g Cl per 100 cc	0.0359	Blank (no excess $CuBr_2$)
$CuBr_2$	0.5640 g Br per 100 cc	0.0625	2 mols. $CuBr_2$ excess
Sugar	5 g per 100 cc	0.0250	this amount same as blank
$MnSO_4$	0.114 g SO_4 per 100 cc 0.114 g SO_4 from Cu salt	0.0250	this amount same as blank
$NaNO_3$	0.8832 g NO_3 per 100 cc	0.0240	5 mols. $NaNO_3$ excess

From these experiments it is seen that a marked effect on the stability of the lake is produced by relatively weak concentrations of the above salts. Copper bromide thus produces more decomposition than copper chloride, as was predicted. Furthermore, in the experiment with equivalent amounts of these salts, where the sodium bromide and chloride were formed by the reaction, and the decomposition was due to them, the same order was noted. $NaNO_3$ produced less decomposition than either of these salts. Sugar and $MnSO_4$ did not produce any decomposition. These results are made clear by considering the work of Spring and Lucion,[1] on the decomposition of salts by means of copper hydroxide. These workers found that the presence even of small amounts of KCl caused a decomposition with a tendency to form compounds varying in composition but containing Cl and copper. They found that KBr was more de-

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[1] Zeit. anorg. Chem., 2, 195 (1893).

composed and they described a basic compound, Cu_2Br_2CuO as produced by this action, in which a reduction of some of the Cu has taken place. Van Bemmelen and Fremy[1] found that a similar decomposition of salts by means of manganese hydroxide was obtained. These workers found that more decomposition was obtained as the concentration of the original solution was increased. The same workers found that the same phenomena were obtained by treating meta-stannic acid with the potassium salts of HNO_3 and H_2SO_4; and that for the same concentration of KNO_3 and K_2SO_4, approximately twice as much decomposition was observed in the case of the sulphate. Thus the behavior of the lake with salts is found to be identical with the behavior of copper hydroxide and other colloidal bases, and indicates that the copper hydroxide is present as such in the copper lake. The decomposition of the lake as measured by the eosin set free, may be explained best on the assumption that the copper hydroxide adsorbs the SO_4 more readily than the eosin radical and the latter is therefore set free. A like explanation is offered in the case of the NO_3 ion, and the known preference for the SO_4 ion over the NO_3 is shown here also.

The $Cu(OH)_2$ produced by decomposition of the lake by shaking with ether and an excess of copper salt, gave the following results on analysis:

The lake contained 1 molecule of copper sulphate in excess, which was obtained by adding the equivalent of 0.1470 gram copper to 0.7497 gram eosin in a total volume of 15 cc. This was shaken for several hours in ether, and the ether was replaced by fresh ether as the solution became concentrated. A gray-white solid remained in the water layer and this was filtered and washed and analyzed for copper. It was found to contain 53.6 percent copper. Considerable amounts of sulphate were found to be present in the resulting solution, although no estimation was attempted. A similar experiment was tried using 3 molecules excess $CuSO_4$ and the re-

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[1] Jour. prakt. Chem., 23, 343 (1881).

sulting gray-white solid was found to contain 53.4 percent copper. Sulphates were also found to be present.

Behavior of the Lake with Acetone

When the copper lake is prepared by precipitation from acetone solutions of $Cu(NO_3)_2$ and sodium eosinate, a brick-red amorphous precipitate is obtained, which is only very slightly soluble in the supernatant liquid. Further dilution of this suspension with acetone gives a red-brown solution which is perfectly stable and which is probably colloidal, in view of the insolubility of crystalline copper eosinate in acetone. The acetone solution is unaffected by an excess of copper salt. When the suspension of the lake in acetone is mixed with approximately an equal volume of water, the suspension clears and a light blue residue is obtained on standing. This precipitate was found to contain 49.0 percent Cu and could not be entirely freed from SO_4 by washing—it was probably a basic sulphate of copper, or $Cu(OH)_2$ with SO_4 adsorbed. Likewise, the suspension of the precipitate of the lake in water when diluted with an equal volume of acetone gave a light colored solution and $Cu(OH)_2$ deposited. It was found that when an excess of copper salt was used in preparing the lake, more $Cu(OH)_2$ was produced. Identical results were obtained by using copper eosinate prepared from $Cu(NO_3)$ dissolved in alcohol, when this suspension was diluted with approximately an equal volume of water. If the suspension of the lake in water were mixed with an equal volume of alcohol, a precipitate of $Cu(OH)_2$ was again obtained. However, there was less precipitate formed in alcohol than in the corresponding cases with acetone. The copper lake precipitated from alcohol solutions, when diluted with alcohol, gave a clear, stable solution, probably colloidal, in view of the insolubility of the crystalline copper eosinate in alcohol. An analysis of the $Cu(OH)_2$ precipitate showed 49.4 percent copper (theoretical for $Cu(OH)_2 = 65.6$); this was probably due to considerable sulphate being retained by the precipitate.

These results with the lake and acetone may be explained as in the case of the ether. The lake is composed of copper hydroxide with eosin adsorbed. Changes in the dilution with the pure liquid cause no change, because the salt is not ionized. When water is added, however, ionization takes place and the lake adsorbs the anion. This sets free the eosin which is in intimate contact with a good solvent and decomposition proceeds. The same explanation is offered for the behavior of the lake with alcohol, and these results argue strongly for the existence of $Cu(OH)_2$ in the lake.

From the results it is seen that the lake produced by the action of an ether solution of eosin upon copper hydroxide behaves as a typical adsorption complex. The amount of eosin thus taken up is very much less than the amount held by the copper in aqueous suspension, probably due to the different physical condition of the copper hydroxide, which has probably undergone agglomeration. The lake when synthesized from copper hydroxide and eosin may be made to contain proportions of copper and eosin, varying from two molecules of copper and one of eosin, to one molecule of copper and two of eosin. These synthetic lakes behave like the ordinary lake produced by supposed double decomposition of copper sulphate and sodium eosinate. The synthetic lakes, especially those containing approximately equivalent proportions of copper and eosin go over, on standing, to the crystalline copper eosinate. The lake produced from copper salt and sodium eosinate also goes over to the crystalline copper eosinate, upon standing. Crystalline copper eosinate is a definite chemical compound, and has none of the properties of the amorphous lake. It is not soluble to any appreciable extent in the solvents which peptonize the lake. It is not affected by an excess of copper or other salts, which do decompose the amorphous lake. The lake produced by adding copper sulphate to sodium eosinate tends to contain copper and eosin in equivalent proportions, although in those experiments where an excess of copper sulphate is used, an excess of copper is found in the lake. This fact may best be explained by adsorption of SO_4 by the $Cu(OH)_2$ of the lake, with a corresponding precipitation of $Cu(OH)_2$ from the copper originally combined with the SO_4. The results obtained are best explained on this basis. Thus, when a substance is added which $Cu(OH)_2$ adsorbs more readily than it does the eosin, the latter is set free. The lake thus behaves in every way as an adsorption complex of copper hydroxide and eosin. A case which is analogous in practically every respect is found in the hydrogel of copper oxide itself. Copper hydroxide has been studied by van Bemmelen.[1] As usually prepared by precipitation from copper salts by means of an alkali, it consists of copper oxide with varying amounts of water, the quantity of the latter constituent has been found to vary continuously in amounts decreasing down to $CuO.H_2O$, without any abrupt change in the vapor pressure of the compound, thus proving that the so-called copper hydroxide really consists of CuO with varying amounts of H_2O adsorbed. Furthermore, a crystalline hydrate was obtained by van Bemmelen having the composition $Cu(OH)_2$, and this had many different properties from the hydrogel. In view of these facts it seems evident that the amorphous lake formed by copper salts and sodium eosinate is not a definite compound, but rather an adsorption complex consisting of copper hydroxide with eosin adsorbed.

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

1. A colorimetric method of analysis was devised for the analysis of eosin compounds.

2. When magnesium oxide is treated with other solutions containing varying amounts of eosin, the typical form of adsorption curve is obtained.

3. When copper hydroxide is treated with ether solutions of eosin in varying amounts, the typical adsorption curve is obtained and there is no indication of a chemical compound, the total amount of eosin taken up being but one-tenth of the amount necessary to form copper eosinate.

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[1] Zeit. anorg. Chem., 5, 466 (1894).

4. The composition of the copper lake produced by copper sulphate and sodium eosinate was studied under conditions in which the concentration of the copper salts was varied over wide limits. The precipitate contained an excess of copper in the cases where an excess of copper salt was employed.

5. It was possible to synthesize lakes from copper hydroxide and eosin, which behaved like the original one. These lakes could be carried into colloidal solution, and all behaved similarly, although the ratio of copper to eosin was varied from two molecules of copper to one of eosin, to two molecules of eosin and one of copper.

6. The transformation of the amorphous lake into crystalline copper eosinate was accomplished for the first time. The crystalline copper eosinate was formed from the lake produced from copper sulphate and sodium eosinate, as well as from the direct synthesis.

7. The properties of the colloidal lake were studied and compared with the entirely different behavior of the crystalline eosinate.

8. A study of the apparent decomposition of the lake in aqueous suspension by means of ether, showed that the eosin was set free from the lake by the greater attraction of the $Cu(OH)_2$ for the anions of certain salts. These anions are adsorbed by the $Cu(OH)_2$, setting free the less weakly adsorbed eosin. The order of the decomposition, due to these adsorbed anions, is the same as is found for other cases of adsorption:

$$SO_4'' > Br' > Cl' > NO_3'.$$

9. The decomposition of the lake by aqueous alcohol and by aqueous acetone was studied and may be best explained on the basis of preferential adsorption of the anions, similar to the case of the ether.

10. The results obtained indicate that the lake produced by adding an aqueous solution of sodium eosinate to a solution of copper sulphate, does not consist of copper eosinate, although the copper and eosin are present in equivalent

amounts. This lake consists of $Cu(OH)_2$, which from the method of formation, contains an equivalent amount of eosin adsorbed.

This work was suggested by Professor Bancroft and has been carried out under his direction. The author takes this opportunity of expressing appreciation of his many suggestions and kind advice in the work.

Cornell University

COOL FLAMES WITH ETHER

BY ALAN LEIGHTON

Over thirty years ago, W. H. Perkin[1] published a paper entitled "Some Observations on the Luminous Incomplete Combustion of Ether and other Organic Bodies."

"When evaporating ether in a shallow vessel on a somewhat strongly heated sand-bath, it is always observed that vapors, irritating to the eyes, are formed. Some time since, when conducting an operation of this kind, in the evening when it was nearly dark, a pale blue flame was seen floating about on the surface of the sand, and yet not igniting the ether which was being evaporated. The experiment was repeated several times, and always with the same result. This phenomenon, which appears to have been almost lost sight of, has been previously observed. It was first noticed by Sir Humphrey Davy,[2] who found that, when a hot spirally wound platinum wire was introduced into a mixture of ether vapor and air, it became red-hot, and in a dark room a pale phosphorescent light was observed above the wire, especially when it ceased to glow. Doebereiner noticed the same thing, but states that the blue lambent flame ceased when the platinum became red-hot. He also remarks that when ether is dropped into a retort heated on the sand-bath to 100° and upwards, or into a platinum capsule exposed to the vapor of boiling water, Leidenfrost's phenomenon (the spheroidal state) is produced, accompanied by a blue flame, visible only in the dark, and not capable of setting fire to other bodies, tear-exciting vapors of lampic acid being formed. As will be seen further on, the temperature of 100°, mentioned by Doebereiner, is insufficient to produce the blue flame. Boutigny, in 1837, observed that this phenomenon took place equally in a metal or porcelain dish, heated to a temperature a little below that

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[1] Jour. Chem. Soc., 41, 363 (1882).

[2] "Gmelin's Handbook of Chemistry," 8, 179–180.

of fusing lead, or about 260°, lampic acid being formed at the same time. Miller also mentions that the glowing extremity of a glass rod or piece of porcelain held over ether, exhibits a small blue flame and forms a large quantity of acid.

"Although the foregoing facts are known, it was thought that it would be interesting to make a few more experiments on this remarkable kind of combustion, and to see if other bodies besides ether were capable of producing the same effect.

"The temperature at which ether begins to burn with this blue flame is about 260°, and any temperature between that and a dull red heat may be used. The higher the temperature, however, the more likely is ordinary combustion to set in.

"There are several ways by which this phenomenon may be produced on a sufficiently large scale to exhibit at lectures. The most simple way is to project ether from a wash-bottle onto a thick iron plate heated nearly to dull redness; but it is better to use a thick iron dish heated over a Bunsen burner, and after the gas has been turned off, or the lamp so screened that no light escapes into the room, to make the jet of ether play on various parts of the surface; in this way a considerable mass of blue flame may be obtained. The best way of showing this flame, however, is to take a copper or iron ball, about 2 or 3 inches in diameter, provided with an eye, so that it may be suspended from a wire, heat it to dull redness, and as soon as it has cooled, so as to be nearly invisible in the dark, place it over a dish about 4 inches in diameter, containing several filter-papers well drenched with ether. As the ball approaches the ether, a beautiful blue flame will form, passing over its heated surface upwards for several inches. The ball may be let right down into the ether without causing ordinary combustion.

"This peculiar combustion of ether may also be shown in a glass tube. A large tube is taken, about 4 cm in diameter, 60 or 70 cm long, bent at right angles about 15 cm from the end, this is fixed with the bend downwards, in a clamp, and some ether poured into it, but not sufficient to prevent a free current of air from passing through the tube. On heating the longer arm of the tube with a Bunsen burner, a draught is instituted, and when the walls of the tube are sufficiently heated, a blue light will be seen on putting out the lamp. If the tube be now shaken to increase the volatilization of the ether, a blue flame will fill the arm of the tube and issue out into the air. It then often enters into ordinary combustion at the opening, and the peculiar effect of the combustion of ether in two manners may be seen at the same time; the blue flame inside the tube is, however, much masked by the luminosity of that outside. The experiment soon afterwards comes to an end by the ordinary flame passing down to the ether, when it is necessary to close the tube to extinguish it.

"This blue flame from ether has a comparatively low temperature. The fingers may be placed in it with impunity. It will not char paper or ignite carbon disulphide, and a lucifer match held in it at first becomes only phosphorescent, and is some time before it is ignited. Ether vapor burning with this blue flame, when in large quantities, or more especially when in a confined space, rapidly increases in temperature and quickly enters into ordinary combustion."

Perkin gives no explanation for the phenomenon and it has evidently been misunderstood because Trautz[1] says that the ether must be heated to 260° in order to give this flame. This cannot be the whole truth because preheating the ether would give a hotter flame if all other conditions were the same. What Perkin did was to drop liquid ether on a hot surface. The rapid evaporation gave a relatively large amount of ether mixed with relatively little air, which was heated to or above the ignition point. Since the combustion was slow, the rise of temperature was not great. On this basis it should be possible to duplicate Perkin's results without the presence of a hot surface, merely keeping the amount of oxygen relatively low and lighting the vapors with a match. This can be done by mixing the ether with a non-inflammable but fairly

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[1] Zeit. phys. Chem., 53, 69 (1905).

volatile liquid such as carbon tetrachloride, or by mixing it with a non-inflammable gas such as carbon dioxide. The form of the experiment differs slightly in the two cases. A blue flame can be obtained by putting some carbon tetrachloride in a crystallizing dish, adding a little ether, and lighting the latter. The hand can be held in this flame with impunity and the flame does not light or char paper. If too much ether is added, the flame will be yellowish at first and it is safer not to put one's fingers in it until the yellow has disappeared completely. If one puts ether in a narrow glass cylinder, and bubbles in carbon dioxide one gets a mixture of ether and carbon dioxide which behaves much like the mixture of ether and carbon tetrachloride. In certain respects this is a prettier experiment than the other because one can make the flame burn in any part of the cylinder that one pleases, by regulating the flow of carbon dioxide. If the flame burns at the mouth of the cylinder, it seems somewhat hotter than the flame due to ether and carbon tetrachloride.

For experimental purposes, carbon bisulphide can profitably be substituted for ether since it gives a much cooler flame. Of course a thermometer held in such a flame does not show the true temperature of the flame; but the readings may be of interest. With carbon bisulphide and carbon tetrachloride in a watch-glass, a thermometer registered 90° if touching the liquid and 140° out in the flame. A reading of 220° instead of 140° was obtained in time when the mixed liquids were poured into a crystallizing dish. With carbon bisulphide and CO_2 in a narrow cylinder a reading of 245° was obtained, while a mixture of ether and carbon dioxide gave a reading of 300° under the same conditions.

Since the temperature of the liquid carbon tetrachloride cannot rise above the boiling-point of the mixed liquids, one gets a striking and harmless experiment by pouring a suitable mixture of carbon bisulphide and carbon tetrachloride into the palm of the hand and then lighting the vapors.

These experiments were suggested by Professor Bancroft.

Cornell University

NEW BOOKS

Photochemistry. *By S. E. Sheppard. 14 × 19 cm; pp. vii + 461. New York: Longmans, Green & Co., 1914. Price: $3.50 net.*—In the preface the author says:

"In the following pages I have endeavored to present a connected, and, in a measure, continuous account of the subject of photochemistry in its modern development. Unification of the scattered elements of this subject is no easy task, in view of the almost inevitable contingency of actino-chemical changes with other thereby recognized and characterized alterations of material systems.

"There has resulted a delay, not without danger, in the attainment of independent status by photo-chemistry, having been for so long ancillary to her elder sisters, thermo- and electro-chemistry, so that only by a masquerade, momentous both for theory and practice, as the science of radio-activity has this Cinderella of the sciences been accorded its due recognition.

"There exists, and is likely to continue, some difference of opinion as to the desirability of incorporating a discussion of photo-physical and radiation phenomena and laws in a work on photo-chemistry. But neglect of this aspect of the question and too narrow a circumscription of its domain can only lead to further delay in the discrimination of a definite body of laws for this science. For this reason the plan has been followed in the present work of discussing at some length certain intensive studies on cardinal points in photochemical change rather than that of enumerating and recording every example of photo-chemical reaction or light-sensitive substance. The aim has been to aid students with examples of working hypotheses helpful in the completer investigation of the economy of any given photo-chemical reaction.

"As such a working hypothesis, the conception that in photo-chemical change singular intermediate complex ions, or, specifically speaking, veritable latent light-images, are formed, appears the most promising. The *singularity* involves concordance of the reaction order or kinetics of their growth and decay with the optical conditions of absorption and emission, the *intermediacy* or metastability of their constitution implies imperfect coincidence of photo-chemical equilibrium with the thermo-dynamically stable equilibria possible to the independent chemical components present.

"Every photo-chemical change is in consequence virtually photographic, the equilibrium to which it tends implies, so to say, a radiation proto-type of a colloid, a characteristic organization radiating from a centre, as the *unit* effect possible. So long as the action is in agreement with the principle of virtual velocities, the change is reversible, the partial chemical transformations tautomeric in type. But any acceleration of the temps of the change involves a loosening of residual affinities in the group which may readily lead to an irreversible transfer of an electron to a depolarizer and consequently to a *per saltum* mutation of the total energy such as the quantum theory of Planck demands. Hence the maximum work developable is as much contingent on the accommodation in space and time of a mutable depolarizer as on the nature of the system insolated, a point emphasized by Grotthuss and recently reiterated by Prof.

Bancroft. On this view the primary or direct photo-chemical change may well be termed catastrophic, and it is only by its coupling with a depolarizer and development as an indirect action that the discontinuous nature of the change is masked by a slow evolutionary process."

The headings of the chapters are: historical; the measurement of light quantities; the energetics of radiation; economic and energetic relations of actual light-sources; the absorption of light; statics and kinetics of photo-chemical change, dynamics of photo-chemical change; special photo-chemistry; radiant matter and photo-chemical change; the genesis of light in chemical change; organic photosynthesis.

The book is a disappointment to the reviewer perhaps because he had expected too much of it. There seems to be no distinct point of view and the author has the unfortunate habit of writing page after page in an involved style without saying anything definite. Typical instances of this will be found on pp. 155–157, 227–230, 245–252, 262–263, 266–267, 319–323, 350–352, 391–392.

As an illustration of this, I quote a rather mild passage, p. 391, from the chapter on the genesis of light in chemical change.

"The extensive technique of the culture and control of flames in detail lies outside the purview of this work. But the word 'culture' is used deliberately to signify that this technique of the study of flames must be necessarily of the same order as that of bacteriological and enzyme chemistry. Flames are not simple chemical species, but physicochemical entities of almost biological standing in the characteristic indetermination of their nature. That is to say, they are very sensitive mobile equilibria of continuously interacting chemical species, in which the act of metathesis is not subordinate to attainment of a static equilibrium, is not monotropic (in essence, exception being made of extrinsic factors which condition practical boundaries or limitations), but is the central and permanent self-reversing condition of their existence. Physically considered, flames are analogous, as singularly constituted transition or intermediate stationary motions of matter between two different states, apparently heterogeneous with each other, but really continuous in the duration of the critical intermediate medium, to 'gels,' which present intermediate, variably permanent transitions of matter between the solid and liquid end-states, and 'vapours,' which present similar permanent becomings or transitions between the liquid and gaseous end-states of matter. In flames, the enduring transition of dominant photo-chemical interest is that representable by the scheme

gas $\rightleftarrows$ electrion or radiant state.

And so well does the ensemble counterfeit immobility that we are likely to misapprehend the fact that the *mobility* of the transition schematized, is the essence of the fact. If we term the pulsation, the to-and-fro movement of an element of matter between two alternative, dynamically incompatible phases (such as gaseous state $\rightleftarrows$ liquid state), a 'physis' or growing, we have in 'gels,' 'vapours,' and 'flames' virtually finite groups of such physes which may be termed 'symphyses,' expressing the fact of a multiplicity of such items growing together syntonically. And as we speak of the *maturation* of a gel, the *saturation* of a vapour, so we might speak of the *naturation* of flames."

Through a curious slip the author considers the color adaptation of the chameleon, p. 335, as a case of Wiener's color adaptation, though the latter applies to substances which tend to assume the color of the incident light, whereas the chameleon assumes the color of the ground which he is on.

Wilder D. Bancroft

Chemistry in America. *By Edgar Fahs Smith. 14 × 21 cm; pp. vii + 356. New York: D. Appleton & Co., 1914. Price: $2.50 net.*—The first chapter opens as follows:

"A review of the contributions of Americans to the Science of Chemistry would be incomplete without a consideration of the publications made in the earliest days in which scientific matters began to interest the people of our country. Before the United States became a republic, interest in such matters was manifested. The members of the venerable American Philosophical Society were most anxious to foster investigations along all lines of scientific endeavor. This is evidenced in a preface to the first volume of the Transactions of that Society, published in 1789, in which the aims of the Society were set forth—to seek the best methods of promoting the fertility of land and of protecting trees and plants from worms and insects, to improve useful animals, to preserve timber, and to ascertain the virtues and use of many plants; and, further, the Society expressly states that it will not confine its efforts wholly to these things, nor will it exclude other useful subjects such as Physics and Chemistry."

Papers by de Normandie, J. Madison, and M'Causlin are cited as illustrating the earliest contributions of Americans to chemistry. After this come two chapters on the Chemical Society of Philadelphia, followed by chapters on Woodhouse, Priestley, Cooper, Maclean, and Robert Hare. A chapter is devoted to the Columbian Chemical Society founded in 1811. The tenth chapter deals with leading chemists as mineralogists, while the eleventh is taken up with sketches of James C. Booth, T. Sterry Hunt, J. Lawrence Smith, and F. A. Genth. The last chapter comes down to the present time with sketches of Wolcott Gibbs, Prescott, Johnson, Mallet, Carey Lea, Cooke, and Willard Gibbs.

The book closes with the following paragraphs:

"The preceding pages contain the most significant efforts of American chemists, extending over a period of a little more than one hundred years. The results compare favorably with those of a like period in the early history of our science in any other country. The earliest contributions represented beginnings. They were carried out when the republic was young. Years of preparation and adjustment followed for the new nation, and then years of internal strife; it is exceedingly gratifying and encouraging to observe that the scientists of the country, including the noble guild of chemists, contributed much to bring the national resources into prominence and usefulness, as well as to guide the educational development of the States.

"To the *Journal of Science*, founded by Silliman, were added *The American Chemist* (1870–, by Charles F. Chandler), the *American Chemical Journal* (1879–, by Ira Remsen), the *Journal of Analytical and Applied Chemistry* (1887, by Edward Hart), the *Journal of Physical Chemistry* (1896, by Wilder D. Bancroft), the *Chemical Engineer* (1904, by R. K. Meade), the Transactions of the American Electro-Chemical Society, the Transactions of the Institute of Chemical Engineers and the most potent factor in chemical affairs—the American Chemical Society, with its admirable journals. All these have fostered the growth and development of chemistry in this country.

"The maintenance of well equipped laboratories in the colleges, as well as the very palatial structures connected with some of the older universities and with the larger state universities, are further evidence of our development along chemical lines.

"It is not the writer's purpose to discuss the investigations which have come from the many working centers of the United States during recent years, that story awaits another narrator; but, if only a desire, on the part of Americans to learn more concerning the place which American chemists occupy in the world's history of chemistry, is awakened, this compilation of facts will not only have been a pleasure but it will have served a worthy purpose."

This is an interesting and valuable book, written in the delightful spirit so characteristic of the author. *Wilder D. Bancroft*

Intermetallic Compounds. *By C. H. Desch. 15 × 22 cm; pp. v + 116. New York: Longmans, Green & Co., 1914. Price: 90 cents net.*—In the introduction the author says: "In the following sections the occurrence of intermetallic compounds as indicated on the equilibrium diagram and determined by the method of thermal analysis is first discussed. This is followed by a short note on the microscopical control of the thermal indications. An account is given of the methods which have been adopted with the object of isolating intermetallic compounds in a pure condition, and of their assumed occurrence as native minerals. So little success has been met with in this direction, however, that our knowledge of the properties of such compounds is mainly derived from a study of the alloys in which they occur. The succeeding sections are therefore devoted to a consideration of the influence which the presence of intermetallic compounds exerts on some of the more important physical properties of alloys. It is also shown that the systematic investigation of certain properties, especially the electrical conductivity and the thermo-electric power, affords the most delicate means in a large number of cases of determining whether chemical combination takes place in a given series or not. An account is then given of the scanty data which we possess as to the crystallographic characters of intermetallic compounds, and of the evidence for the existence of compounds in liquid alloys, and the concluding section reviews the theoretical aspect of the subject."

The book is an interesting one and the only serious criticism to be made is on the paragraph, in which the author assumes definite compounds as occurring in a series of solid solutions. The author says, p. 17, that "the two opposing views refer only to the molecular condition of the solid solutions concerned. On the one view the metals are present at least in a large part in the form of compound molecules, on the other, they are free." This is quite wrong. The reviewer has never stated that the six series of solid solutions in the copper-zinc alloys are due to copper and zinc alone. He has taken the ground that we have no general way of telling what are the constituents of any given series of solutions and that it is more profitable to admit our ignorance than to postulate the existence of arbitrarily selected compounds. *Wilder D. Bancroft*

The Theory of Heat Radiation. *By Max Planck. Translated by Morton Masius. 15 × 21 cm; pp. v + 225. Philadelphia: P. Balkiston's Son & Co., 1914. Price: $2.00 net.*—This is a translation of the second German edition. In the preface the author says:

"The main fault of the original treatment was that it began with the classical electrodynamical laws of emission and absorption whereas later on it became evident that, in order to meet the demand of experimental measurements, the assumption of finite energy elements must be introduced, an assumption which is in direct contradiction to the fundamental idea of classical electrodynamics. It is true that this inconsistency is greatly reduced by the fact that, in reality, only mean values of energy are taken from classical electrodynamics, while, for the statistical calculation, the real values are used; nevertheless the treatment must, on the whole, have left the reader with the unsatisfactory feeling that it was not clearly to be seen, which of the assumptions made in the beginning could, and which could not, be finally retained.

"In contrast thereto, I have now attempted to treat the subject from the very outset in such a way that none of the laws stated need, later on, be restricted or modified. This presents the advantage that the theory, so far as it is treated here, shows no contradiction in itself, though certainly I do not mean that it does not seem to call for improvements in many respects, as regards both its internal structure and its external form. To treat of the numerous applications, many of them very important, which the hypothesis of quanta has already found in other parts of physics, I have not regarded as part of my task, still less to discuss all differing opinions."

The five sections of the little volume are entitled: fundamental facts and definitions; deductions from electrodynamics and thermodynamics; entropy and probability; a system of oscillators in a stationary field of radiation; irreversible radiation processes. *Wilder D. Bancroft*

The Viscosity of Liquids. *By A. E. Dunstan and F. B. Thole. 15 × 22 cm; pp. v + 89. Longmans, Green & Co., 1914. Price: 90 cents net.*—The subject is treated under the headings: the development of a working formula; the measurement of viscosity; the measurement of the viscosity of pure liquids prior to 1895; the measurement of the viscosity of pure liquids subsequent to 1895; the viscosity of liquid mixtures; viscosity of electrolytic solutions; the viscosity of colloids; the relation between viscosity and chemical constitution; some applications of viscosity.

One reason for making a distinction between measurements of viscosity before and after 1895 is that the later experiments were subsequent to those of Thorpe and Rodger. The chapter on the viscosity of colloids is interesting both for what it does and does not contain. There is no discussion at all of what would happen if the more viscous phase were the external one and yet this is a very important matter in the case of true emulsions. On the other hand, the chapter does contain a discussion of the work of Wolfgang Ostwald and of Hatschek, as well as paragraphs on the properties of colloidal solutions of soap, nitrocellulose, and rubber.

In the chapter entitled "Some Applications of Viscosity," the authors say:

"The value of a physical property in the eyes of the average chemist depends on its applicability to problems which arise in the various branches of chemistry and which sometimes cannot be definitely solved by purely chemical methods. Mention need only be made of the application of refractivity and absorption spectra to the classical controversies concerning the constitutions of ethyl acetoacetate and of isatin and of the work of Patterson, Lowry, and others on the connection between rotatory power and velocity of chemical reaction. Since viscosity is so highly a constitutive property, it may and has been applied to a number of problems arising in physical, inorganic, and organic chemistry, and has proved particularly useful in certain cases such as determining the constitution of the acetaldehyde phenylhydrazones where chemical evidence is not available."

Wilder D. Bancroft

The Sugars and Their Simple Derivatives. *By John E. Mackenzie. 16 X 23 cm; pp. vii + 242. Philadelphia: J. B. Lippincott Co., 1914. Price: $2.25 net.* —In the preface the author says:

"The carbohydrates are among the most important of all chemical compounds, from several points of view. They form the main portion of the diet of most animals. They are the raw material for many industries. Yet comparatively little is known concerning the more complicated carbohydrates, though much study has been devoted to them. On the other hand, the simple carbohydrates, the sugars, have been investigated to such effect that the chemical configuration of the majority of them has been elucidated.

"The following pages are based on a course of lectures first given at Birkbeck College, London, in 1903, and subsequently at the University of Edinburgh. In addition to students of pure chemistry, others interested in medicine, brewing and distilling, sugar manufacture, etc., attended these lectures. On this account more attention has been devoted to such subjects as metabolism, fermentation, and the manufacture of sugars than would have been the case otherwise. It is hoped that the book may serve as a companion to works on physiological chemistry and to technological works on brewing, distilling, sugar manufacture and sugar analysis."

The author discusses the preparation and properties of sucrose, maltose, lactose, glucose, and glucosamine. He then takes up the dioses, trioses, tetroses, pentoses, methylpentoses, aldohexoses, and ketohexoses; after which come twenty pages devoted to disaccharides, trisaccharides, tetrasaccharides, and glucosides. The last two chapters are entitled fermentation and metabolism.

The book seems to be a careful compilation of data, with relatively few errors. On p. 27 the author says that "the heat of solution of sugar in water is positive for all concentrations at temperatures between 15° and 25°, but becomes negative above 50°. As early as 1680, Boyle observed that a freezing mixture could be made by mixing sugar and snow." There is no necessary relation between these two sentences and it is a pity that a false impression should be conveyed. It is also unfortunate not to distinguish between heat of solution and heat of dilution. The work of Fischer and of Nef is given in considerable detail and Hudson's work on milk sugar has not been overlooked.

Wilder D. Bancroft

ADSORPTION AND STABILIZATION[1]

BY J. C. BLUCHER AND E. F. FARNAU

A question which for decades has off and on occupied the attention of chemists, industrial and academic, is the nature of the process of dyeing. For almost every other kind of physico-chemical phenomenon we have formulated laws, or invented satisfactory theories and hypotheses. The nearest approach yet made to a satisfactory working hypothesis concerning dyeing is the adsorption theory—one which seemingly throws into the limbo of uselessness the previous theories of mechanical entanglement, chemical combination, and solid solution.

Objections to earlier theories of dyeing are numerous and valid.

(1) The mechanical theory assumes that the particles of dye are simply entangled in the dyed fibre. Obviously this cannot explain why a substance is taken up from true solution; moreover, the theory takes no cognizance of the reversibility of the equilibrium. This is undoubtedly the weakest theory of dyeing yet proposed.

(2) When we deal with the theory of chemical combination of the dye with the fibre we are met by a greater obstacle. For in many cases the color of the dyed fibre is in agreement with the color of chemical compounds of the dye. But it is absurd to think, for instance, that charcoal can exhibit both acidic and basic properties when it takes up, in one case basic, and in another case acid dyes. Also, for reversible equilibrium this theory requires the presence of the components, fibre, dyestuff and solvent in four phases—undyed fibre, dyed fibre (that is, compound of fibre and dyestuff), solution, and vapor—a three-component body in a four-phase state, having one degree of freedom, let us say temperature. Then

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[1] A paper read before the Division of Physical and Inorganic Chemistry at the Cincinnati meeting of the American Chemical Society, April, 1914.

at constant temperature there should be but one concentration of dyestuff in the liquid for which the equilibrium would hold. This is easily disproved by experiment.

(3) But by far the most formidable rival with which the modern adsorption theory has had to contend is that of solid solution. This theory was introduced by Witt[1] in 1890–91. To support his theory, Witt cited the fact that dyes which have a different color in solution from that which they possess in the solid state, impart to the dyed substance not the color of the solid but that of the solution. Also, fluorescent solutions made from non-fluorescent solids give fluorescent dyeing. Substantive (or direct) colors were assumed to be shared between the fibre and the solution in much the same way as resorcinol is shared between water and ether, all of which was very fine, but dyes do not seem to obey the laws of distribution of substances between two immiscible solvents—laws which are shown by the work of Nernst to be quite accurate for dilute solutions. Walker and Appleyard[2] were largely instrumental, by their work on the adsorption of picric acid from water and alcohol, solutions by silk, in disproving the theory of solid solution; and a short review of their work would not be out of place.

When the molecular complexity of the dissolved substance is the same in both solvents, there is for simple cases, a constant ratio of concentrations when equilibrium is reached, the ratio being entirely independent of the amounts of the substance and solvents originally taken, provided the solutions be dilute. Thus, succinic acid distributes itself between water and ether[3] in the concentration-ratio of 5.2 to 1. When, however, the molecular complexity of the dissolved substance is not the same in the two solvents, there is no constant distribution ratio, the latter depending upon the original quantities present. But there is a more complex relationship which obtains. If the molecular weight of the substance in the first solvent is

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[1] O. N. Witt: Färberzeitung, 1890–91.

[2] Walker and Appleyard: Jour. Chem. Soc., 69, 1334 (1896).

[3] Berthelot and Jungfleisch: Ann. chim. phys., [4] 26, 396 (1872).

n times as great as its molecular weight in the second solvent, then, when equilibrium is attained, the nth power of the concentration in the first solvent will bear a constant ratio to the concentration in the second solvent, *i. e.*, $c_1^n/c_2 = K$.

According to the solid solution theory these laws should hold good for dyeing. And the formula, $c_f^n/c_w = K$, should hold if the dye possesses different molecular complexity in the fibre and in the water, where c_f is the concentration of the dye in the fibre, c_w the concentration of the dye remaining in the dye-bath, and n the ratio of the molecular weight of the substance in the water to its molecular weight in the fibre. Georgievics[1] and Schmidt,[2] the former from observations on dyeing silk with indigo carmine, the latter from observations on the adsorption of picric acid by cellulose and of eosin and malachite green by silk, applied the above ratio to the case of dyeing. Walker and Appleyard found the relation $c_f^{2.7}/c_w = 35.5$, to hold for picric acid and silk. This entails the consequence that the molecule of picric acid in aqueous solution is on the average 2.7 times as great as the molecule of picric acid dissolved in silk. This, however, cannot be the case, for a consideration of the freezing point and the electric conductivity of picric acid solutions indicates that the molecule is not only not greater than is represented by its molecular formula but less than this, owing to the electrolytic dissociation. The solid solution theory can receive no support from these experiments. But formulae of the kind mentioned do apply in practically all cases of adsorption.

(4) There remains, then, the fourth theory—namely, that of adsorption.

Numerous investigators have found that the concentrations of the dye in the fibre and in the bath vary continuously. Pelet-Jolivet[3] finds such to be the case in the adsorption of NaOH and H_2SO_4 and tannin by wool; Walker and Apple-

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[1] Georgievics: Monatsheft für Chemie, 15, 707 (1894).

[2] Schmidt: Zeit. phys. Chem., 15, 60 (1894).

[3] Pelet-Jolivet: "Die Theorie des Färbeprozesses" (1910).

yard[1] in the adsorption of picric acid by silk; Sanin[2] in the adsorption of tannin by wool; Georgievics[3] in the dyeing of silk with indigo carmine, and cellulose with methylene blue; and Pelet-Jolivet[4] gives considerable data on the dyeing of wool, silk, and cotton with various dyes. Also, the process of dyeing is reversible, although sometimes this is not readily apparent. No dyed substance will withstand unlimited washing.

Although such experiments show the non-validity of the solid solution theory from the standpoint of distribution ratio, no explanation was offered to account for the facts advanced by Witt, relating to the colors of the dyestuffs taken up by the fibre. Jacquemin[5] demonstrated the dyeing of wool and silk by rosaniline base from a colorless ammoniacal solution; Sisley[6] also reports that silk is dyed red from colorless solutions of magenta in water or toluene, an experiment easily verified. And, in general, only the free base or free acid of the dyestuff is taken up by the fibre, which nevertheless takes on the color of the salt of the dyestuff.

In order to account for these apparent anomalies, Bancroft[7] has advanced a stabilization theory of dyeing, in support of which he cites the facts that, although hydrous copper oxide is transformed at 100° into black copper oxide, the former when adsorbed on wool[8] is stable in boiling water, and that hydrous copper oxide in the presence of small amounts of manganous salts[9] is likewise stable at 100°.

It is the purpose of the present paper to cite further ex-

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[1] Walker and Appleyard: Loc. cit.

[2] Sanin: Zeit. Kolloidchemie, 10, 82 (1912).

[3] Georgievics: Akad. Wiss. Wien., 103, II*b*, 589 (1894); 104, II*b*, 309 (1895).

[4] Pelet-Jolivet: Loc. cit.

[5] Jacquemin: Comptes rendus, 82, 261 (1876).

[6] Sisley: Bull. Soc. chim. Paris, [3] 23, 865 (1900).

[7] Bancroft: Jour. Phys. Chem., 18, 118 (1914).

[8] Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 2nd Ed., 1, 59 (1910).

[9] Tommasi: Bull. Soc. chim. Paris, [2] 37, 197 (1882); Comptes rendus, 99, 37 (1884).

amples of the same type, substantiating the theory that in many cases adsorption may appreciably stabilize a substance.

In a paper read before the Cincinnati Section of the American Chemical Society in 1904, Benedict[1] unconsciously utilized the phenomenon of stabilization in a very delicate test for nickel. He found that "if NaOH be added in excess to a cobalt solution, a dark blue precipitate is at first formed, which is usually regarded as a basic salt. If nickel be entirely absent, this salt changes almost instantaneously to a bright pink compound, *viz.*, the normal cobaltous hydroxide. If, however, nickel is present, this change of color is retarded, the length of time increasing with the amount of nickel present. This test is extremely rapid, yet its rapidity is fully equalled by its delicacy. Mere traces of nickel can be detected." Benedict's assumption of the formation of an intensely blue compound, the so-called nickel cobaltite, is not borne out by experiment. A larger proportion of nickel does not increase the intensity of the blue color, but merely retards the rate of its change to pink. According to the present theory, the hydrous nickel oxide stabilizes the blue modification of hydrous cobalt oxide.

The chemical composition of the blue precipitate obtained on adding insufficient caustic alkali to cobalt sulphate was established by Hantzsch.[2] After washing with cold water until the filtrate was free from sulphates the precipitate was found to contain 15 percent of SO_4; but four treatments with boiling water decreased this without change of color to 4 percent, corresponding to the formula $Co(OH)_2.{}^1/_{24}CoSO_4$. It need scarcely be stated that this is a case of adsorption, similar to that observed under like conditions with nickel, copper, and magnesium sulphates. In terms of the present theory, the adsorbed cobalt sulphate has stabilized the blue modification of hydrous cobalt oxide. It is interesting to note that Hantzsch assigns to the blue and red modifications the structural formulae, $CoO—H_2O$ and $Co(OH)_2$, respectively.

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[1] Benedict: Jour. Am. Chem. Soc., 26, 695 (1904).

[2] Hantzsch: Zeit. anorg. Chem., 73, 304 (1912).

Bayliss[1] found that hydrous aluminium oxide could be dyed red from a blue colloidal solution of the free acid of Congo red. Hydrochloric acid was added to Congo red to precipitate the free acid, which when diluted formed a blue colloidal solution. Freshly prepared hydrous aluminium oxide was added. In the cold the colloidal oxide was dyed blue, but upon heating the color changed to red. Bayliss accounts for the color change on the ground that the blue free acid is transformed into the red aluminium salt;—and thus reverts to the chemical theory of dyeing. According to the present theory, the red Congo acid, although instable in aqueous suspension, is stabilized by the hydrous aluminium oxide. Experiments are now under way in which attempts are being made to prepare the instable free acids of the acid dyestuffs. If these dye the hydrous aluminium oxide the same color as the free acids, any objection to the present explanation will be removed.

Tommasi[2] investigated the effect of salts upon the decomposition temperatures of blue hydrous copper oxide.

Upon repeating Tommasi's experiments with hydrous copper oxide and manganous sulphate, we were led to question whether the stabilization was a property peculiar to manganous sulphate, or whether other salts produced the same effect. Accordingly the sulphates of Mn, Zn, Ni, Al, Cr and the chlorides of Co, Mg, and Hg were employed. In all cases, except with mercuric chloride, positive and very striking results were obtained.

The method of experimentation was as follows: Normal solutions of all the various reagents were used. One cc amounts of the copper sulphate solution were measured into test tubes from a burette and diluted with 8–10 volumes of distilled water. Then to each test tube was added exactly 1 cc of the sodium hydroxide solution from a burette, and the solution well shaken. A blue, gelatinous hydrous copper

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[1] Bayliss: Proc. Roy. Soc., 84, 881 (1911).

[2] Tommasi: Loc. cit.

oxide was thus obtained. Then the different amounts of "stabilizers" were added in drops from a pipette, and the test tubes again shaken. The test tubes were then placed in a beaker of boiling water and the results shown in the tables were obtained. In each series of experiments a blank test, without stabilizer, was made. In every case this showed blackening inside of half a minute, thus making the stabilizing action of the salts used more striking by contrast.

SERIES I (5 MINUTES)—$MnSO_4$
1 cc $CuSO_4$ + 1 cc NaOH

$MnSO_4$	Results
0 drops	blackened in 1/2 minute
1 drop	very slight darkening
2 drops	no change
3 drops	no change
4 drops	no change
5 drops	no change

SERIES II (10 MINUTES)—$MnSO_4$
1 cc $CuSO_4$ + 1 cc NaOH

$MnSO_4$	Results
0 drops	blackened in 1/2 minute
1 drop	blackened appreciably
2 drops	trace of blackening
3 drops	no change
4 drops	no change
5 drops	no change
6 drops	very slight brown tinge

SERIES III (5 MINUTES)—$MnSO_4$
1 cc $CuSO_4$ + 1 cc NaOH

$MnSO_4$	Results
0 drops	deep black in one minute
3 drops	no change
0 drops	deep black in one minute
3 drops	no change
0 drops	deep black in one minute
3 drops	no change

SERIES IV (10 MINUTES)—$ZnSO_4$

1 cc $CuSO_4$ + 1 cc NaOH

$ZnSO_4$	Results	
0 drops	black in 1/2 minute	
1 drop	black in 10 min.	no change in 5 min.
2 drops	black in 10 min.	
3 drops	slightly black in 10 min.	
4 drops	slightly black in 10 min.	
5 drops	gray in 10 min.	
6 drops	gray in 10 min.	

SERIES V (5 MINUTES)—$ZnSO_4$

1 cc $CuSO_4$ + 1 cc NaOH

$ZnSO_4$	Results
0 drops	black in 1/2 min.
3 drops	no change
0 drops	black in 1/2 min.
3 drops	no change
0 drops	black in 1/2 min.
3 drops	no change

SERIES VI (10 MINUTES)—$NiSO_4$

1 cc $CuSO_4$ + 1 cc NaOH

$NiSO_4$	Results
0 drops	black in 1/2 min.
1 drop	appreciable darkening in 2 min.
2 drops	no change
3 drops	no change
4 drops	no change
5 drops	no change
6 drops	no change

SERIES VII (5 MINUTES)—$NiSO_4$

1 cc $CuSO_4$ + 1 cc NaOH

$NiSO_4$	Results
0 drops	black in 1/2 min.
3 drops	no change
0 drops	black in 1/2 min.
3 drops	no change
0 drops	black in 1/2 min.
3 drops	no change

SERIES VIII (10 MINUTES)—$CoCl_2$
1 cc $CuSO_4$ + 1 cc NaOH

$CoCl_2$	Results
0 drops	black in $^1/_2$ min.
1 drop	black in 10 min.
2 drops	no change
3 drops	no change
4 drops	no change
5 drops	no change
6 drops	no change

SERIES IX (5 MINUTES)—$CoCl_2$
1 cc $CuSO_4$ + 1 cc NaOH

$CoCl_2$	Results
0 drops	black in $^1/_2$ min.
2 drops	no change
0 drops	black in $^1/_2$ min.
2 drops	no change
0 drops	black in $^1/_2$ min.
2 drops	no change

SERIES X (10 MINUTES)—$Al_2(SO_4)_3$
1 cc $CuSO_4$ + 1 cc NaOH

$Al_2(SO_4)_3$	Results	
0 drops	black in $^1/_2$ min.	
1 drop	black in 10 min.	ppt. made lighter in color
2 drops	no change	
3 drops	no change	
4 drops	no change	
5 drops	no change	
6 drops	no change	

SERIES XI (5 MINUTES)—$Al_2(SO_4)_3$
1 cc $CuSO_4$ + 1 cc NaOH

$Al_2(SO_4)_3$	Results
0 drops	black in $^1/_2$ min.
2 drops	no change
0 drops	black in $^1/_2$ min.
2 drops	no change
0 drops	black in $^1/_2$ min.
2 drops	no change

SERIES XII (10 MINUTES)—$Cr_2(SO_4)_3$

1 cc $CuSO_4$ + 1 cc NaOH

$Cr_2(SO_4)_3$	Results
0 drops	black in 1/2 min.
1 drop	black in 10 min.
2 drops	no change
3 drops	no change
4 drops	no change
5 drops	no change
6 drops	no change

SERIES XIII (5 MINUTES)—$Cr_2(SO_4)_3$

1 cc $CuSO_4$ + 1 cc NaOH

$Cr_2(SO_4)_3$	Results
0 drops	black in 1/2 min.
2 drops	no change
0 drops	black in 1/2 min.
2 drops	no change
0 drops	black in 1/2 min.
2 drops	no change

SERIES XIV (5 MINUTES)—$MgCl_2$

1 cc $CuSO_4$ + 1 cc NaOH

$MgCl_2$	Results
0 drops	black in 1/2 min.
3 drops	no change

SERIES XV—$HgCl_2$

1 cc $CuSO_4$ + 1 cc NaOH

$HgCl_2$	Results
0 drops	black in 1/2 min.
2 drops	black in 1 min.
3 drops	black in 2 min.
4 drops	black in 2 min.
5 drops	black in 2 min.
6 drops	black in 2 min.

SERIES XVI

1 cc $CuSO_4$ + 1 cc NaOH

NaOH		Results
	0 drops	black in 1/2 min.
+3 drops	$MnSO_4$ 3 drops	brown in 1/2 min.[1]
+3 drops	3 drops	brown in 1/2 min.[1]
+3 drops	3 drops	black in 1/2 min.[1]
+2 drops	2 drops	black in 1 min.
+2 drops	2 drops	black in 1 min.
+2 drops	2 drops	black in 1 min.
	$CuSO_4$ 3 drops	black in 3 min.
	$CuSO_4$ 2 drops	black in 2 min.
	HCl 2 drops	black in 1 min.
	$ZnSO_4$ 2 drops	no change
	NaOH 3 drops	black in 1/2 min.

Quite recently, Finch[2] has investigated the coagulation of cupric oxide jellies, and finds that sulphates, but not manganous salts, increase their permanence. It would seem likely, therefore, that if coagulation of these jellies is a case of dehydration, the dehydration of coagulated hydrous cupric oxide with formation of black cupric oxide must be considered a matter altogether different.

Walker and Appleyard made the anomalous observation that although silk is not dyed from a benzene or carbon tetrachloride solution of picric acid, silk previously dyed from a water or alcohol solution and dried, is not faded by benzene or carbon tetrachloride. As a tentative explanation Bancroft suggests that this is because the silk is not wetted by benzene. Our own results on the action of common solvents on fibres of silk, observed under the microscope, indicate that silk is wetted by these solvents, or by their solutions of picric acid. Furthermore, preliminary results on dyeing of silk by picric acid from mixtures of organic solvents would seem to indicate that it is merely a matter of rate of attainment of equilibrium. Silk is quite markedly dyed from solutions of picric acid in

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[1] Remained greenish brown

[2] Finch: Jour. Phys. Chem., 18, 26 (1914).

carbon tetrachloride containing only one percent by volume of absolute alcohol.

The following fairly consistent hypothesis might be suggested to account for this result. Picric acid, like most other dyes, exists in two forms; in this case the one colored, the other colorless. In water or alcoholic solution the two forms are in equilibrium, and so reversible equilibrium between the liquid and silk exists. But a carbon tetrachloride solution of picric acid, at least at ordinary temperatures and at 60°, contains so little of the colored modification that reversible equilibrium is reached with difficulty. The case of the benzene solution is complicated by presence of the benzene-picric acid compound, but this probably has no dyeing properties. One could also prophesy the same results with ligroin or chloroform solutions,—in fact with any colorless solution of picric acid. The effect of solvent on tautomeric change is exemplified in the cases of nitroso-benzene and the pseudo-nitrols, which as solids are colorless, but yield colored solutions.

Whatever may be the ultimate explanation of this phenomenon, its formal classification as a case of stabilization will still be valid.

Summary

1. The stabilization theory of Bancroft is confirmed by further examples.

2. These include the stabilization of blue hydrous cobalt oxide by nickel oxide and by cobalt sulphate, of the red acid of Congo red by hydrous aluminium oxide, and of blue hydrous copper oxide by a number of metallic hydroxides.

3. Common organic solvents and their picric acid solutions wet silk.

4. The apparent irreversibility in dyeing of silk from benzene solution of picric acid is probably a question of tautomerism as well as of slowness of attainment of equilibrium.

New York University
March, 1914

THE PHOTOLYSIS OF POTASSIUM IODATE

BY J. HOWARD MATHEWS AND HARRY A. CURTIS

Introduction

Recently it was noted in this laboratory that potassium bromate apparently decomposes quite rapidly in light of short wave lengths. A quartz vessel containing a solution of potassium bromate and a little starch potassium iodide as an indicator became blue on a few seconds' exposure to the light from a quartz-mercury vapor lamp. Potassium chlorate and potassium iodate gave the same results. These reactions seemed so promising that it was decided to investigate them quantitatively if possible. The investigation has led to the consideration of several problems in photochemistry, and in one direction to a problem quite out of the field of photochemistry, as will be indicated below.

A few preliminary tests soon made it clear that potassium bromate alone does not decompose rapidly in solution, and that the observed result was due to the oxidation of the potassium iodide by the oxyhalogen salt under the influence of light of short wave length. If potassium bromate solution were exposed for a few seconds and then removed from the light, it would give no blue color upon the addition of the potassium iodide-starch indicator. Nor would the starch-potassium iodide solution become blue on short exposure, although a longer exposure (a few minutes usually) would, of course, give blue, due to the well-known photo-oxidation of potassium iodide in the presence of air. The mixture of the two salts was far more sensitive to the light than either of them alone. The same was found to be true in the case of the iodate and chlorate.

It has been found that this reaction is an excellent one for lecture demonstration purposes, especially because of the fact that it is not very sensitive to the light of such wave lengths as ordinary glass will transmit. The details of this demonstration experiment are given below.

In the present paper only the photolysis of potassium iodate and its reaction with potassium iodide will be considered. Similar investigations with potassium chlorate and potassium bromate are under way in this laboratory and the results will appear later.

Lecture Demonstration Experiment in Photochemistry

Dissolve about one-tenth of a gram of potassium iodate in five hundred cc of distilled water. Add to this two cc of a one percent iodide solution and two cc of a one percent starch solution. Pour one-half of this mixture into a three hundred cc quartz flask and the other half into a similar flask of ordinary glass. Expose the two solutions at equal distances on either side of a quartz-mercury vapor lamp. In a few seconds the solution in the quartz flask will become a deep blue, while the solution in the glass flask remains quite colorless.

The amounts of reagents may be varied within very wide limits, the only effect being to change the time required for the appearance of the blue color. For example, the iodate used has been varied from 0.001 gram to one gram, and the iodide from 0.01 gram to one gram without changing the result except as to time. The variations in time required give no trouble practically, since the extreme change in the above limits was less than a minute using a "110-volt" lamp.

The effect of carbon dioxide on the reaction is large, as will be shown below, but with ordinary distilled water no trouble from this source has been experienced.

The Photolysis of Potassium Iodate

On long exposure to light of short wave lengths, potassium iodate in solution slowly decomposes, liberating iodine. The reaction may be followed by titrating the liberated iodine with standard sodium thiosulphate solution.

In the experiments described below, Merck's potassium iodate was used. This was recrystallized three times from distilled water, discarding each time the first portion of crystals to separate and the mother liquor. The purified iodate was tested for chlorate by converting to the iodide and then applying the chromyl chloride test for chlorine. Negative results were obtained on duplicate tests.

In determining the amount of iodine liberated, a 0.001 *N* solution of thiosulphate was used, this solution being always protected from carbon dioxide by a soda-lime tube. It was found best to add a slight excess of the standard thiosulphate in titrating, and then at once titrate back to a faint blue end point with standard iodine solution. In calculating the amount of thiosulphate required, a correction was always made for the amount of iodine required to give a faint blue end point in the volume of solution used. It would be desirable to determine also the amount of iodate actually decomposed by a direct determination of the potassium iodate content of the solution before and after illumination. A simple calculation shows, however, that the amount of iodate corresponding to the iodine liberated is not much larger than the unavoidable error which enters in the determination of the iodate. It was necessary, therefore, to depend entirely upon the iodine liberated as a measure of the progress of the reaction.

In each of the experiments described below, two hundred cc of tenth normal potassium iodate solution were used. Because of the small amount of iodine liberated it was necessary to titrate the whole solution after each period of illumination. This rendered the investigation rather a long and tedious one.

Apparatus Used

The following arrangement of apparatus shown, in part, in Fig. 1, has proved very satisfactory in studying photochemical reactions in solution.

The quartz-mercury vapor lamp A, is mounted over a water thermostat, B, provided with thermometer, electric temperature regulator, etc. The quartz flask C, containing the reaction mixture, is mounted as near the lamp as desired, and kept at constant temperature by allowing water from the perforated ring D, to flow down over it. This water is taken from the thermostat and delivered to the perforated ring by a small centrifugal pump, E, driven by an electric motor. The reaction mixture in C is agitated by the stirrer F, which is driven by the pulley G, the latter being carried on an extension of the shaft operating the large stirrer in the thermostat.

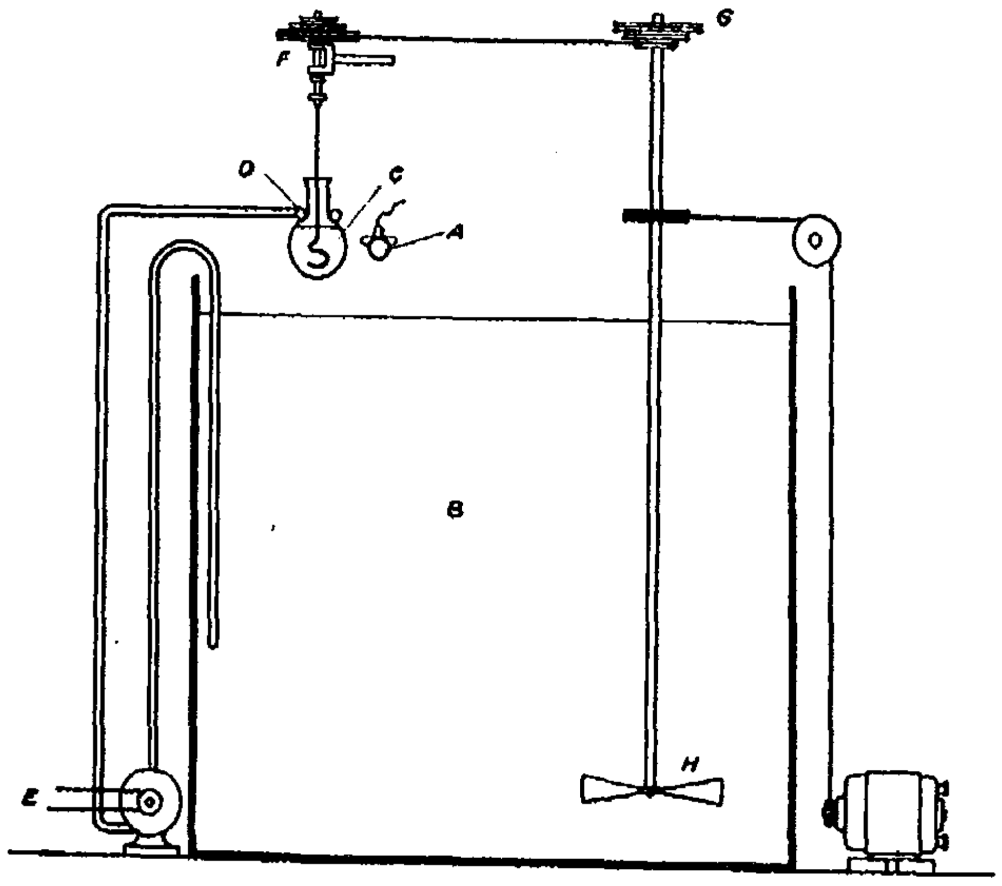

Fig. 1

When the flask C is to be left open to the air, an ordinary glass stirrer may be used. It is often desirable, however, to keep the solution in the flask C out of contact with air, or saturated with some particular gas. In the latter case the excellent device proposed by Plotnikow may be substituted for the simple stirrer. This device is shown in Fig. 2, where the quartz reaction flask C is drawn on a larger scale.

The apparatus is set up without the mercury in the seal L, and the gas to be used is delivered through the tube M until all the air in C has been replaced. Mercury is then poured in to make the seal, and the three-way cock N is turned so as to bring the gas burette O, filled also with the gas to be used, in connection with the flask C. By means of the leveling tube the pressure in the flask C may be kept constant at any pressure near that of the atmosphere. If the stirrer be rotated at a high speed, gas will be drawn in through the hole P, and thrown out into the liquid, keeping the latter always saturated with the gas.

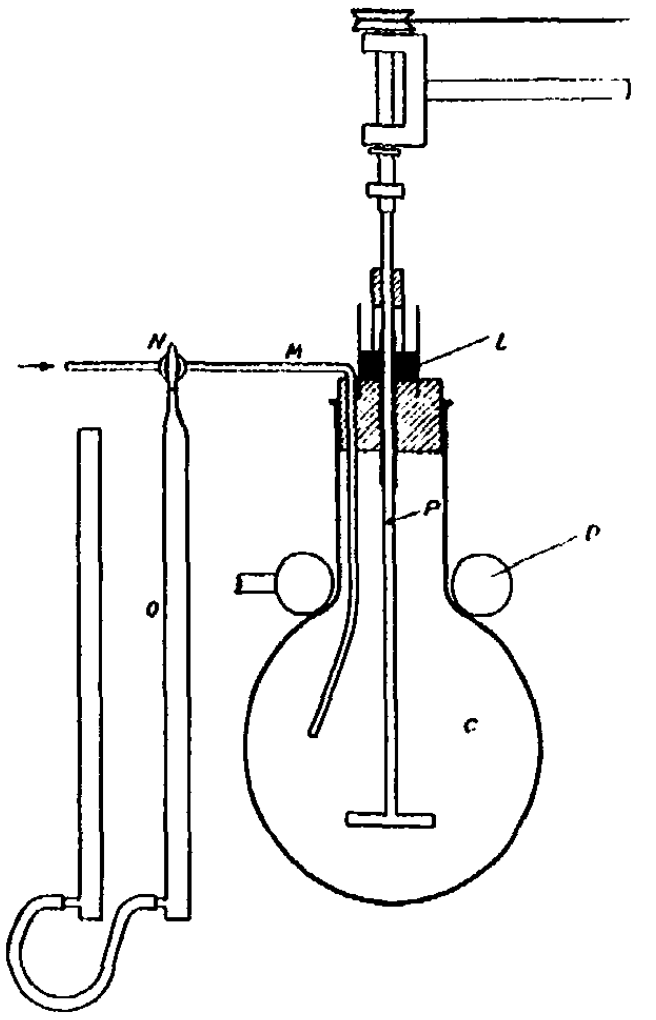

Fig. 2

Rate of Photolysis of Potassium Iodate Solution in the Presence of Air

In Table I, and in Fig. 3, are given the data for the photolysis of tenth normal potassium iodate solution, the flask C being left open to the air. Two hundred cc of tenth normal iodate solution were used each time, and the temperature held at 30°. In titrating with the thiosulphate solution as dilute as 0.001 *N* it is not to be expected that duplicate determinations will yield exactly the same titer, nor that a very smooth curve will result when these numbers are plotted on as large a scale as has been used in Fig. 3.

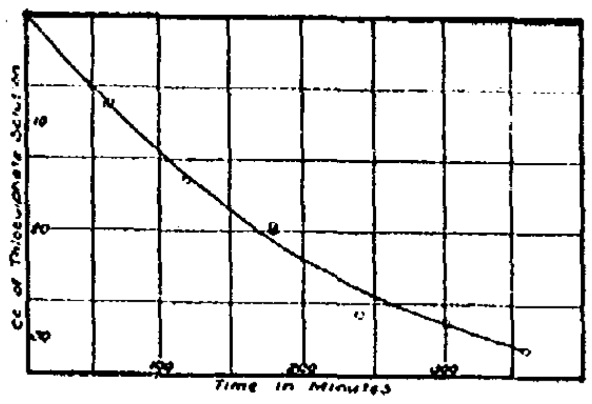

Fig. 3

TABLE I

Time in minutes	cc $Na_2S_2O_3$	Time in minutes	cc $Na_2S_2O_3$
61	8.4	180	19.7
63	8.2	240	27.6
120	15.3	300	28.3
180	19.4	360	30.9

The Influence of Oxygen on the Photolysis of Potassium Iodate Solution

In attempting to follow the reaction between a mixture of potassium iodate and potassium iodide under the influence of light, it was not possible at first to get concordant results. It was finally noticed that the rate of the reaction could be greatly increased by shaking the reaction mixture with air before insolating it. This fact seemed to indicate that the oxygen of the air was disturbing the reaction, and suggested at once the possibility that the photolysis of the iodate alone was also influenced by air. To decide this point regarding the iodate, a solution of potassium iodate was prepared in water which had been boiled for an hour and then cooled in an atmosphere of pure nitrogen. The reaction flask was fitted with a stirrer carrying a mercury seal and was filled with pure nitrogen. The iodate solution was then forced into the flask and the excess of nitrogen allowed to escape through the mercury seal, so that the reaction flask finally contained an air-free solution of potassium iodate under an atmosphere of nitrogen. (The rather elaborate apparatus for accomplishing the above result is not described, for reasons which appear below.) The iodate solution was now insolated for 168 minutes, and it was found that it required 11 cc of the standard thiosulphate solution to titrate the liberated iodine, whereas the amount interpolated from Fig. 3 for 168 minutes is about 19 cc. This result apparently indicated that air influences the reaction, but it seemed strange that the effect was not greater than was actually found. Many attempts were now made to prepare an iodate solution so free from air that no decomposition of the iodate would occur on insolation. Long-continued boiling of the solution under reduced pressure before illumination would always greatly reduce the rate of photolysis, and on two occasions no iodine was obtained, although several similar experiments gave positive results, the amount of iodine being always very small, however. The fact that the decomposition could be reduced so nearly to zero seemed to indicate that no decomposition would occur if the last trace of air could be removed from the solution, but it seemed impossible to do this. As will appear later, our efforts were directed toward the removal of a substance which takes no part in the reaction.

Finding it impossible to obtain checking results by this plan, it was decided to keep the concentration of the oxygen constant by keeping the solution always saturated with oxygen. The Plotnikow saturation device was, therefore, substituted for the ordinary stirrer and pure oxygen used. It was now found that no decomposition occurred. The next step was obvious; substitution of carbon dioxide for oxygen gave positive results at once.

The Effect of Carbon Dioxide on the Photolysis of Potassium Iodate Solution

Carbon dioxide greatly increases the rate of photolysis of potassium iodate in solution. Table II and the solid-line curve of Fig. 4 present the data for the decomposition of potassium iodate in a solution kept saturated with carbon dioxide. The broken-line curve of Fig. 4 represents the rate of photolysis of the potassium iodate when the solution was exposed to the air, the curve being here plotted on the same scale as used for the solid-line curve.

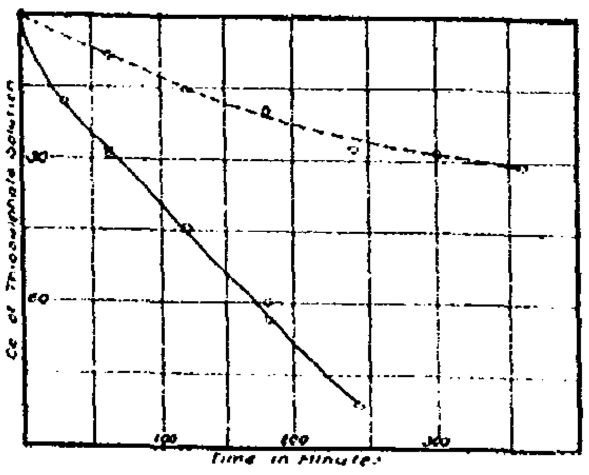

Fig. 4

TABLE II

Time in minutes	cc thiosulphate	Time in minutes	cc thiosulphate
30	18.3	180	59.8
30	18.4	180	63.2
62	28.7	243	81.1
62	28.2	—	—
120	44.3	—	—
122	44.5	—	—

Order of the Reaction when Carbon Dioxide is Present

Inspection of Fig. 4 shows that the amount of iodine liberated is a linear function of the time of insolation, *i. e.*, the reaction apparently does not follow the mass law.[1] While it is true that the decomposition here is practically linear with respect to time of insolation, it is not permissible to draw conclusions regarding the order of the reaction from such data as are available in Table II, a point which the following consideration will make clear: For the two hundred cc of

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[1] This case is sometimes loosely expressed by saying that the reaction is of the zero order, *i. e.*, the rate of reaction is independent of the concentration.

tenth normal iodate solution it would require twenty liters of the standard thiosulphate solution to titrate the iodine if it were all liberated. Since the maximum amount of thiosulphate solution actually required for any titration was less than one hundred cc, it is evident that less than one two-hundredth of the total amount of iodate was decomposed during the longest period of insolation, *i. e.*, for the purposes of the mass law calculations, the iodate concentration of the iodate would be considered as constant, and this makes the rate constant, regardless of the order of the reaction. The fact that it is not possible to judge correctly the order of a reaction when the amount transposed is very small as compared with the total amount present must be especially noted in photochemical research where, on account of the small effect of light on most reactions, the amount of material transformed in the photochemical reaction is apt to be but a small fraction of the total amount present. It was pointed out in our paper on the photolysis of hydrogen peroxide[1] that the decomposition of the peroxide is a linear function of the time of insolation when the concentration of the peroxide is higher than about 1.5 percent, although the reaction is clearly of the first order when the concentration is small.

Knowing the effect of carbon dioxide on the photolysis of the iodate, it is now possible to explain the decomposition curve obtained when the flask was left open to the air (Fig. 3). The iodate solution would absorb carbon dioxide from the air but slowly, while the amount in the solution would grow less, since the carbon dioxide is certainly used in the reaction. The rate of photolysis would, therefore, decrease, a fact which was very puzzling when the data for Fig. 3 were first obtained. By keeping the solution always saturated with carbon dioxide, this factor became constant and the decomposition curve then became a straight line, as was to be expected from the relatively small amount of decomposition.

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[1] Jour. Phys. Chem., 18, 166 (1914).

The Reaction between Potassium Iodate, Potassium Iodide and Carbon Dioxide in the Absence of Light

From a solution containing both potassium iodate and potassium iodide, carbon dioxide at once liberated iodine. This fact is not often mentioned in the literature, and has been entirely neglected in certain investigations of the reaction between these salts in the presence of other acids. For example, Dushman,[1] in his study of the reaction between these salts in the presence of acetic acid, kept all his solutions under an atmosphere of carbon dioxide and must, therefore, have had the effect of carbonic acid superposed upon that of acetic acid. In fact, with carbon dioxide in the solution the acetic acid may be omitted entirely and the reaction will still proceed rapidly. We have studied the reaction between potassium iodate, potassium iodide and carbon dioxide; the results of this investigation will appear later, since they do not fall under the head of photochemical research with which the present paper deals. The investigation is mentioned here because of its bearing on the problem of the photolysis of potassium iodate, since a knowledge of the reaction between potassium iodate and potassium iodide in the presence of carbon dioxide makes it possible to formulate what appears to be a logical explanation of the photolysis of potassium iodate and the influence of carbon dioxide upon this reaction.

Theory of the Photolysis of Potassium Iodate in a Solution Containing Carbon Dioxide

Potassium iodate decomposes under the influence of light, yielding oxygen and potassium iodide. The iodide formed is at once oxidized by the potassium iodate in the presence of the carbon dioxide. In a solution saturated with carbon dioxide, the speed of the second reaction is far higher than that of the first, so that the reaction velocity measured will be that of the photolysis of potassium iodate. The equations might be written:

$$KIO_3 = KI + 3O$$
$$5KI + KIO_3 + 6CO_2 + 3H_2O = 6KHCO_3 + 6I$$

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[1] Jour. Phys. Chem., 8, 453 (1904).

If this theory be the correct one, oxygen should be liberated, and even though the amount of potassium iodate decomposed be small, there should be an appreciable volume of oxygen liberated. To test this point experimentally, a solution of potassium iodate was insolated in a quartz flask so arranged as to collect any gas which might be liberated. When this was done, there was a slow but steady accumulation of gas which on testing was found to be insoluble in sodium hydroxide solution but readily soluble in alkaline pyrogallol.

Concerning the Influence of Light on the Reaction between Potassium Iodate and Potassium Iodide in the Presence of Carbon Dioxide

Light increases the speed of this reaction, but it has not been possible so far to make any progress toward a quantitative examination of the reaction. The number of variable factors is so large as to make the problem extremely complex. Potassium iodide alone is decomposed by light, the reaction being affected by oxygen and possibly also by carbon dioxide; potassium iodate is decomposed by light, the reaction being affected by carbon dioxide; potassium iodate and potassium iodide react if carbon dioxide be present, the reaction being conditioned by at least three concentrations. Combine all these variables in one reaction, and then add the effect of light on the whole mixture, and the problem becomes so complex that progress toward a quantitative study of the photochemical reaction involved seems almost hopeless. The reaction, however, is an excellent one for demonstrating the role of wave length in photochemical reactions, as has been pointed out.

Summary

1. An apparatus suitable for the study of photochemical reactions in solution has been described.

2. A lecture demonstration experiment suitable for showing the role of wave length of the light used in photochemical reactions has been described.

3. The photolysis of potassium iodate in solution has been studied quantitatively, with the results enumerated under Nos. 4, 5, 6, 7, below.

4. When the photolysis of potassium iodate is carried out with the solution exposed to air, the rate of photolysis slowly decreases.

5. Iodine is not liberated when the insolated solution is kept saturated with oxygen.

6. Carbon dioxide greatly increases the rate of photolysis of potassium iodate in solution.

7. The rate of photolysis of potassium iodate in a solution kept saturated with carbon dioxide is linear when the amount of iodine liberated is small compared with the total amount present in the iodate. Under such circumstances it is not possible to determine correctly the order of the reaction involved.

8. A theory of the way in which the photolysis of potassium iodate occurs has been suggested.

9. Light accelerates the reaction between potassium iodate, potassium iodide and carbon dioxide, but the reaction is very complex in the presence of light and has not been investigated quantitatively.

NOTE.—Since preparing the above article for publication, the paper by Oertel[1] on the photolysis of chlorates, bromates and iodates has come to our attention through the pages of *Chemical Abstracts*, the original article having escaped our notice. Oertel has pursued the investigation along quite different lines from those followed in the present paper, but we take this opportunity to give reference to his paper.

Laboratory of Physical Chemistry
University of Wisconsin
May, 1914

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[1] Biochem. Zeit., 60, 480 (1914); Chem. Abstr., 8, 1746 (1914).

THE TERNARY SYSTEMS, POTASSIUM—PHOSPHORIC ACID—WATER AND AMMONIA—PHOSPHORIC ACID—WATER

BY E. G. PARKER[1]

A question of considerable importance in fertilizer chemistry today is whether or no a concentrated fertilizer, that is, a fertilizer containing a high percent of the so-called plant foods, can be economically produced and used.

A concentrated fertilizer can obviously be made by mixing in the desired proportions the various ingredients, which process would require the production of each ingredient separately and a final mixing. The object of this work was to ascertain whether stable chemical compounds containing the three most important of fertilizer constituents, potash, phosphoric acid, and ammonia, exist at ordinary temperatures. Although the subject has at present been anything but exhaustively investigated, and further work is at present being carried on with the hope of either a positive or a negative final conclusion, many valuable observations were made which makes desirable the publication of the present report of progress.

The work was carried on in conjunction with other fertilizer investigations in this laboratory under the direction of Dr. Frank K. Cameron.

The two three-component systems, namely, K_2O—P_2O_5—H_2O and NH_3—P_2O_5—H_2O, were first investigated, and isotherms obtained for each system. The temperature chosen was 25° Centigrade, and was kept constant in a thermostat to an accuracy of one-tenth of one degree throughout the experiment. These systems have already been explored, in part, by D'Ans and Schreiner.[2]

Potassium—Phosphoric Acid—Water

Bottles containing various amounts of orthophosphoric acid and potassium hydroxide in solution and in contact

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[1] Scientist, Soil Laboratory Investigations Bureau of Soils.

[2] J. D'Ans and O. Schreiner: Zeit. phys. Chem., **75**, 95 (1910).

with a solid phase were placed in a thermostat and allowed to rotate until equilibrium was established. Portions of the liquid and solid phases at equilibrium were removed and examined.

TABLE I—COMPOSITION OF SOLID AND LIQUID PHASES

Liquid phase		Solid phase			
K	PO_4	Percent K	Percent PO_4	Formula	Optical property
Mols per 1000 gr. of solution	Mols per 1000 gr. of solution				
1.40	8.56	16.13	82.00	$KH_2PO_4.H_3PO_4$	—
1.47	6.74	16.75	80.55	$KH_2PO_4.H_3PO_4$	—
2.31	5.00	25.62	67.23	KH_2PO_4	Uniaxial(—)
1.89	3.20	28.05	69.18	KH_2PO_4	Uniaxial(—)
1.78	2.60	28.20	69.00	KH_2PO_4	Uniaxial(—)
1.51	1.81	—	—	KH_2PO_4	Uniaxial(—)
1.46	1.46	27.90	67.50	KH_2PO_4	Uniaxial(—)
2.31	1.84	27.80	68.70	KH_2PO_4	Uniaxial(—)
2.61	1.99	—	—	KH_2PO_4	Uniaxial(—)
3.06	2.25	28.00	67.50	KH_2PO_4	Uniaxial(—)
3.20	2.28	28.40	68.10	KH_2PO_4	Uniaxial(—)
3.98	2.67	28.40	67.50	KH_2PO_4	Uniaxial(—)
5.22	3.24	28.10	65.90	KH_2PO_4	Uniaxial(—)
5.33	3.33	—	—	KH_2PO_4	Uniaxial(—)
5.67	3.41	28.30	66.00	KH_2PO_4	Uniaxial(—)
6.38	3.69	28.80	64.10	KH_2PO_4	Uniaxial(—)
6.80	3.92	28.50	62.90	KH_2PO_4	Uniaxial(—)
7.23	3.73	—	—	K_3PO_4	Biaxial(+)
7.79	3.66	—	—	K_3PO_4	Biaxial(+)
8.56	3.42	—	—	K_3PO_4	Biaxial(+)
8.81	2.92	—	—	$K_3PO_4.3H_2O$	Biaxial(—)
7.14	2.07	—	—	$K_3PO_4.3H_2O$	Biaxial(—)
7.18	2.09	—	—	$K_3PO_4.3H_2O$	Biaxial(—)
9.19	0.48	43.90	34.10	$K_3PO_4.3H_2O$	Biaxial(—)
9.23	0.46	43.60	33.70	$K_3PO_4.3H_2O$	Biaxial(—)
9.41	0.38	—	—	$K_3PO_4.3H_2O$	Biaxial(—)
9.79	0.23	43.85	34.30	$K_3PO_4.3H_2O$	Biaxial(—)
9.80	0.24	—	—	$K_3PO_4.3H_2O$	Biaxial(—)
9.48	0.32	—	—	$K_3PO_4.3H_2O$	—
9.76	0.24	42.60	1.37	$KOH.2H_2O$	—
9.76	0.22	42.60	0.70	$KOH.2H_2O$	—
9.77	0.12	—	—	$KOH.2H_2O$	—

Phosphoric acid was determined according to the method of B. Schmitz.[1] Potassium was determined by precipitation as potassium chlorplatinate. Some of the solid phases were primarily examined by chemical analysis, but on collecting sufficient data on their optical properties, some were identified microscopically by Mr. William H. Fry of this Bureau. The results of the examination of the various liquid and solid phases are given in the preceding table.

From these results isotherms were plotted with mols of K per 1000 grams of solution as ordinates and mols of PO_4 per 1000 grams of solution as abscissae (see Fig. 1).

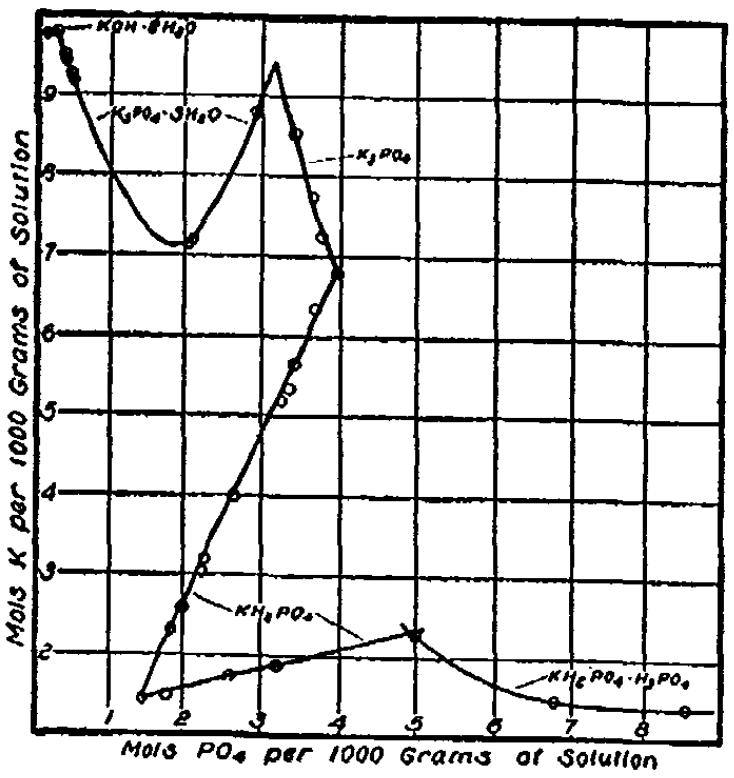

Fig. 1—Concentration isotherms for the three-component system K_2O—P_2O_5—H_2O at 25° C

From Table I and Fig. 1 it appears that the stable solid phases in contact with solutions containing potassium and orthophosphoric acid at 25° C are,

$KH_2PO_4.H_3PO_4$
KH_2PO_4
K_3PO_4
$K_3PO_4.3H_2O$
$KOH.2H_2O$

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[1] Page 434 of Treadwell and Hall's "Analytical Chemistry," Vol. II (1913).

The branch of the curve representing KH_2PO_4 has, at a concentration of about 1.46 mols of K and 1.46 mols of PO_4 per 1000 grams of solution, an apparent sharp break, and the addition of either potassium or phosphoric acid at this point increases the solubility of the monopotassium phosphate. It was thought possible that the monopotassium phosphate might exist in more than one modification, a transition taking place at about 25° C. Investigation by means of the dilatometric method showed this not to be the case (see Fig. 2).

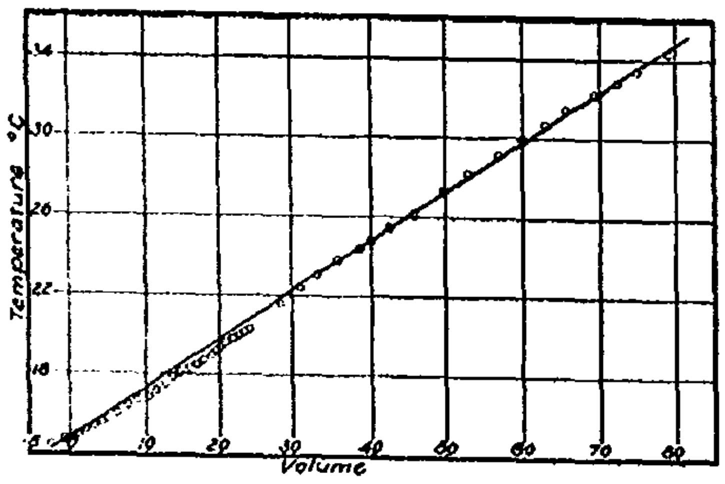

Fig. 2—Curve showing the change in volume of KH_2PO_4 with increasing temperature

So that no doubt might exist that the solid phases stable on both sides of this apparent sharp point were chemically the same, they were all analyzed and plotted on a triangular diagram. The composition of the solid phases always corresponds to the formula KH_2PO_4. (Point S—see Fig. 3.)

The existence of an actual break or an intersection in the curve would be a contradiction of the phase rule. The probability is that instead of a sharp break in the solubility curve for the phosphate with the formula KH_2PO_4, it goes through an undetectable minimum at this point as suggested by J. D'Ans and O. Schreiner.[1] The significance of the fact that the ratio of potassium to phosphoric acid is 1 : 1 at this minimum is not apparent.

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[1] J. D'Ans and O. Schreiner, Zeit. phys. Chem., **75**, 95 (1910).

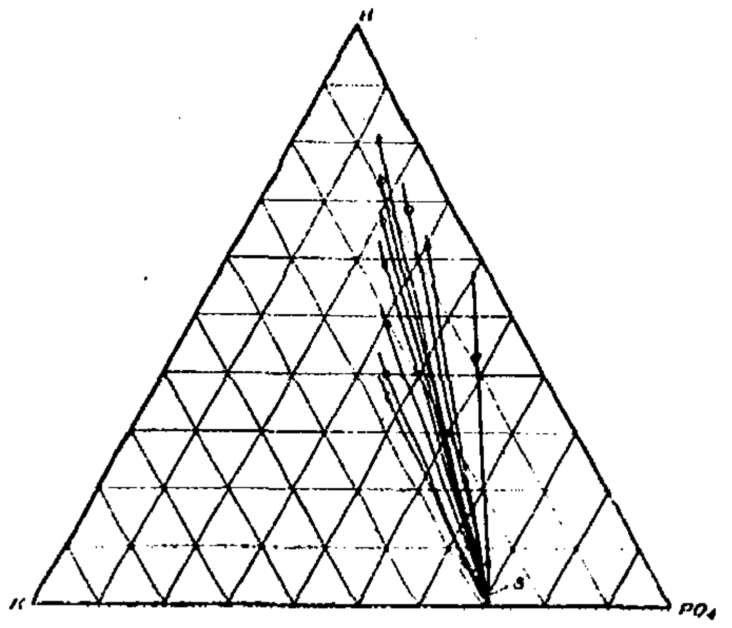

Fig. 3—Graphical representation for the determination of the composition of a solid phase

Ammonia—Phosphoric Acid—Water

Bottles containing various amounts of ammonia and orthophosphoric acid in solution and in contact with a solid phase, were allowed to rotate in a thermostat until equilibrium was established. Portions of the solid and liquid phases at equilibrium were removed and examined.

Ammonia was determined according to a standard method.[1]

Some of the solid phases were identified by means of the microscope.

The results of the examination of the various liquid and solid phases are given in Table II.

From these results isotherms were plotted with mols of NH_4 per 1000 grams of solution as ordinate and mols of PO_4 per 1000 grams of solution as abscissae (see Fig. 4).

From Fig. 4 and Table II it appears that the stable solid phases in contact with solutions containing ammonia and orthophosphoric acid at 25° C are

$(NH_4)H_2PO_4$
$(NH_4)_2HPO_4$
$(NH_4)_3PO_4.3H_2O$

On the branch of the curve representing $(NH_4)H_2PO_4$

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[1] Page 59 of Treadwell and Hall's "Analytical Chemistry," Vol. II (1913).

we find that the same sharp break is present as in the case of the KH_2PO_4. The break in this case is not quite as sharp, indicating that the explanation offered for the case of the monopotassium phosphate to be correct. Along the curve for $(NH_4)_3PO_4.3H_2O$ from the point C to the left ammonia is given off from the liquid, hence the curve as it stands in the figure is not theoretically correct, as pressure was considered constant throughout the experiment. It may, however, be assumed to be practically so.

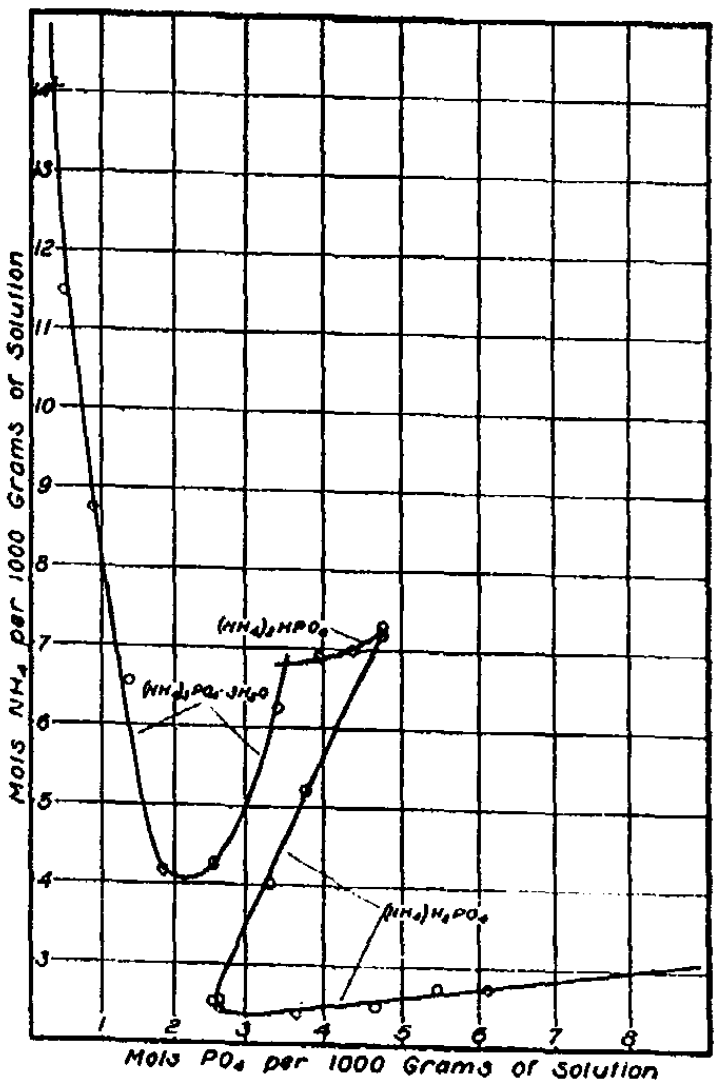

Fig. 4—Concentration isotherms for the three-component system NH_4—P_2O_5—H_2O at 25° C

These two isotherms may now be considered to be in planes at right angles to each other, and from these an isotherm for the four component system K_2O—NH_3—P_2O_5—H_2O may be continued and be represented in space.

TABLE II—COMPOSITION OF SOLID AND LIQUID PHASES

Liquid phase		Solid phase	
NH_4	PO_4	Formula	Optical property
Mols per 1000 grams of solution	Mols per 1000 grams of solution		
2.77	6.09	$(NH_4)H_2PO_4$	Uniaxial(—)
2.75	5.44	$(NH_4)H_2PO_4$	Uniaxial(—)
2.50	4.61	$(NH_4)H_2PO_4$	Uniaxial(—)
2.40	3.62	$(NH_4)H_2PO_4$	Uniaxial(—)
2.45	2.64	$(NH_4)H_2PO_4$	Uniaxial(—)
2.58	2.57	$(NH_4)H_2PO_4$	Uniaxial(—)
2.58	2.67	$(NH_4)H_2PO_4$	Uniaxial(—)
4.04	3.30	$(NH_4)H_2PO_4$	Uniaxial(—)
5.23	3.77	$(NH_4)H_2PO_4$	Uniaxial(—)
7.21	4.75	$(NH_4)H_2PO_4$	Uniaxial(—)
7.30	4.76—	$(NH_4)_2HPO_4$	Biaxial
7.01	4.38	$(NH_4)_2HPO_4$	"
6.90	3.95	$(NH_4)_2HPO_4$	"
6.27	3.41—	$(NH_4)_3PO_4.3H_2O$	Biaxial(—)
4.28	2.57	$(NH_4)_3PO_4.3H_2O$	Biaxial(—)
4.19	1.83	$(NH_4)_3PO_4.3H_2O$	Biaxial(—)
6.59	1.33	$(NH_4)_3PO_4.3H_2O$	Biaxial(—)
8.75	0.87	$(NH_4)_3PO_4.3H_2O$	Biaxial(—)
11.48	0.43	$(NH_4)_3PO_4.3H_2O$	Biaxial(—)
14.08	0.41	$(NH_4)_3PO_4.3H_2O$	Biaxial(—)

Bottles containing varying amounts of potassium hydroxide, ammonia, and orthophosphoric acid in solution and in contact with a solid phase were placed in a thermostat and allowed to rotate until equilibrium was established. Portions of liquid phases were then analyzed, with the results of the analyses given in Table III.

From these results a curve was plotted with mols K per 1000 grams of solution as abscissae and mols of NH_4 per 1000 grams of solution as ordinates (see Fig. 5) which curve would be a projection of an isotherm in space, on a plane at right angles to the two planes on which the isotherms for the three-component systems $K_2O—P_2O_5—H_2O$ and $NH_4—P_2O_5—H_2O$ were plotted.

TABLE III—COMPOSITION OF LIQUID PHASE

K	NH_4	PO_4
Mols per 1000 grams of solution	Mols per 1000 grams of solution	Mols per 1000 grams of solution
1.00	2.87	3.16
1.19	2.97	3.31
1.31	2.88	3.31
1.45	2.89	3.36
1.60	2.93	3.41
1.76	2.65	3.35
1.94	2.62	3.26
2.18	2.34	3.23
2.50	2.08	2.23
2.62	2.03	3.21
2.86	1.85	3.21
4.54	1.53	3.59
4.87	1.20	3.84
4.90	1.56	3.96
4.96	1.43	4.04
5.60	1.32	4.00
5.44	1.21	3.92
5.88	1.12	4.02

In order that the point of lowest vapor pressure of the system might be determined a solution containing orthophosphoric acid, ammonia, and potassium was allowed to stand over sulphuric acid in a closed space at 25° C until both the sulphuric acid and the solution had come to a constant weight, and a solid in examinable amounts had separated from the solution. The solution was then analyzed and found to have a concentration of 1.81 mols of NH_4, 4.95 mols of K, and 3.96 mols of PO_4 per 1000 grams of solution. This concentration corresponds to a break in the curve shown in Fig. 5, Point A. The solid in contact with this solution, which presumably should contain some of each of four different solid phases, was examined under the microscope. One or more of these solid phases present was undoubtedly instable in the air as ammonia was rapidly given off. Solids having the same optical property as KH_2PO_4 and K_3PO_4 were identified under the microscope. It is possible that other substances might have approximately the same optical properties as KH_2PO_4 and K_3PO_4, but it is more probable that this point of minimum vapor pressure is at an invariant point to be represented in space, at which there are four solid phases in contact with the solution of the above concentration, which are K_3PO_4, KH_2PO_4, two double salts, one or both of which is instable in the air, or a double salt, which is instable, and a solid solution. It is obvious, however, that if a compound of potassium, ammonia and phosphoric acid stable at ordinary temperatures is to be obtained, it is necessary to work with solutions more acid than those represented by the isotherm, the projection of which is given in Fig. 5.

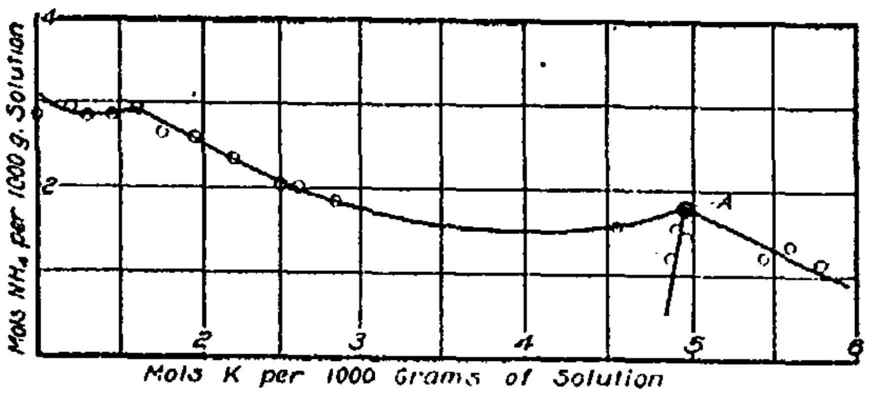

Fig. 5—Projection of some of the concentration isotherms fo the four-component system K_2O—NH_3—P_2O_5—H_2O at 25° C

The economic production of a stable compound of this kind, if possible, would, under present commercial conditions, require the use of potassium chloride, and work on the conditions required for the separation of such a compound, employing potassium chloride, either from an aqueous solution or an alcoholic solution as suggested by Mr. P. J. Fox[1] of this laboratory, is now contemplated.

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[1] P. J. Fox.

THE RADIOACTIVITY OF SOME COLORADO SPRINGS

BY HERMAN SCHLUNDT

The determinations recorded in tabular form below were obtained during the summer of 1913. The measurements were conducted in the field at the springs. The measuring instrument employed was a Mache-Meyer fontactometer.[1] Its ionization chamber had a volume of nearly 15 liters. The electrostatic capacity of the electrode system was 10.42 cms. The voltages corresponding to the scale readings of the charged leaves of the electroscope were furnished by the maker. The instrument was also calibrated in this laboratory by Mr. L. A. Bell. His value of the electrostatic capacity was 10.45, and the curve he obtained by plotting volts against scale readings coincided with the graph of the maker's values. The instrument was also standardized with known quantities of radium emanation separated, (1) from uraninite, and (2) from standard solutions of radium bromide kindly furnished by Professor Boltwood. As a result of a considerable number of determinations by Mr. L. A. Bell,[2] who employed different methods of separating the emanation, and several by the author we found that a fall of potential of one volt per minute represents the emanation in equilibrium with 2.95×10^{-10} grams of radium, when readings were taken from two to three minutes after the introduction of the gas. Readings taken three hours later, when the activity has reached a maximum value, gave a value of 1.80×10^{-10} grams of radium per volt fall per minute.

The readings in the field were generally made from two to three minutes after the introduction of the water or gas sample. Hence the values recorded in the last column of

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[1] Phys. Zeit., 10, 860 (1909).

[2] Dissertation for the degree of Master of Arts, Univ. Missouri (1914).

the tables were obtained by using the calibration factor 2.95×10^{-10} grams radium per volt per minute. This factor depends to some extent upon the density of the air in the ionization chamber when observations are made. The value used was obtained for a barometric pressure of 740 mm of mercury and room temperature, but at the altitude of the springs the barometric pressure averaged 610 mm. At the higher altitude a fall of one volt per minute would represent a slightly greater quantity of emanation.

The activities are also expressed in Mache units. These values represent the ionization currents per liter of water, or gas, expressed in electrostatic units multiplied by 1000. They were calculated by use of the formula:

$$i = \frac{q \times c}{300 \times t \times v}$$

where q is the potential fall in volts during the interval of time t, expressed in seconds, c, the electrostatic capacity of the electrometer, 10.45, and v, the volume in liters of the water or gas sample used for the determination. The recorded activities in Mache units have been corrected (1) for the emanation remaining in solution in the water sample in the ionization vessel;[1] (2) for the ionization produced by the active deposit resulting from the decay of the emanation during the time it remains in the ionization chamber;[2] and (3) for the normal air leak of the instrument.

The activities of the gas samples refer to volumes which have been reduced to standard temperature and pressure. For details concerning the collection and transfer of gases in the field see Schlundt and Moore, Bulletin No. 395, U. S. Geological Survey. For the sake of comparison the activities of several well known springs have been added.

The activities represent radium emanation. What proportion of the emanation represents dissolved radium salts in the spring waters was not determined, but presumably

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[1] Hofmann: Phys. Zeit., 6, 337 (1905).

[2] Schmidt: Ibid., 6, 561 (1905).

Table I—Activities of Spring Waters

Name of spring	Temp.	Locality	Mache units	Grams Ra × 10^{10}
Eldorado	21.0	Eldorado Springs	3.25	19.6
Blue Bell	12.5	Blue Bell Canon	0.43	2.7
Red Rock	12.3	Boulder	2.49	14.7
Boulder Mineral	14.5	Crisman	3.74	22.4
Navajo	—	Manitou	3.36	20.1
Shoshone	14.9	Manitou	8.25	47.3
Navajo Geyser	13.0	Manitou	4.49	26.7
Iron Soda	14.7	Manitou (Mansion House)	3.74	22.4
Ouray	15.1	Manitou	1.41	8.45
Little Chief	17.2	Manitou	3.16	19.5
Ute Iron	10.2	Manitou	3.25	20.0
Manitou Soda	14.5	Manitou	3.04	17.6
Cheyenne Soda	12.7	Manitou	2.32	13.1
Seven Minute Geyser	12.8	Manitou	1.98	11.5
Ute Chief Magnetic	13.7	Manitou	1.35	8.2
Iron Springs Geyser	11.2	Manitou	2.34	14.0
Soda Spring	14.8	Steamboat Springs	0.43	2.55
Bath House Spring	39.5	Steamboat Springs	0.21	1.2
Navajo	13.0	Steamboat Springs	0.32	1.9
Iron	23.8	Steamboat Springs	2.39	14.3
Craddock	—	Glenwood Springs	5.4	30.6
Mühlbrunnen	39.2	Karlsbad	31.5	Mache and Meyer
Johannabad	30.0	Baden	4.54	Mache and Meyer
Vauquelin	—	Plombieres	9.4	Curie and Laborde
D'Alun	—	Aix-les-Bains	10.5	Curie and Laborde
Chomel	—	Vichy	0.7	Curie and Laborde
Elizabeth Brunnen	9.6	Kreuznach	13.0	Kurz
Koch Brunnen	—	Wiesbaden	2.3	Henrich
Apollinaris	9.2	Yellowstone Park	10.4	Schlundt and Moore
Nymph	—	Yellowstone Park	2.26	Schlundt and Moore

TABLE II—ACTIVITIES OF SPRING GASES

Name of spring	Locality	Mache units	Grams Ra per liter × 10^{10}
Navajo	Manitou	8.03	48.1
Navajo[1]	Manitou	13.3	—
Shoshone	Manitou	31.2	205
Navajo Geyser	Manitou	8.0	47
Iron Soda	Manitou	2.6	15.4
Iron Springs Geyser	Manitou	4.77	28.8
Soda	Steamboat Springs	3.46	20.5
Bath House	Steamboat Springs	1.32	7.9
Milk (or lithia)	Steamboat Springs	1.79	10.9
Iron	Steamboat Springs	9.05	51.5
Sulphur	Steamboat Springs	1.59	8.8
Ink	Steamboat Springs	0.81	4.7
Terrace No. 1	Steamboat Springs	8.32	50.5
Nymph	Yellowstone Park	6.25	Schlundt and Moore
Bench	Yellowstone Park	118.3	Schlundt and Moore
Fish Cone	Yellowstone Park	39.9	Schlundt and Moore
Mühlbrunnen	Karlsbad	94.2	Mache and Meyer
Chomel	Vichy	18	Curie and Laborde
Schützenhof	Wiesbaden	50	Henrich
Johannabad	Baden	16.6	Mache and Meyer

[1] Shedd: Proc. Col. Sci. Soc., 10, 257 (1913).

but a very small fraction of the emanation present in any of the springs can be attributed to radium salts carried in solution. This conclusion is based upon some tests of stored samples of "Manitou" water. Its activity was not more than three percent that of the fresh water. No tests were conducted on the water residues or the spring deposits. At Steamboat Springs the escaping gases from three of the springs were tested for thorium emanation, but the results were negative. The activity of the water from Glenwood Springs was determined on a sample collected by the owner and shipped to Columbia. The value given represents the initial activity.

In 1905, Headden[1] described a very interesting group of radioactive springs in Delta County, Colorado, known as the Doughty Springs. The sinter deposited close to the springs is unique in that it consists largely of barium sulfate. Headden found the sinter to be quite radioactive. At the time, Professor Headden had the kindness to furnish us with a sample of the sinter. The air dry sample contained approximately 87 percent of barium sulphate. Its radium content was determined by a modification of the fusion method of Joly and was found to be 14.8×10^{-10} grams of radium per gram of material, which corresponds to nearly 0.5 percent of uranium in a natural mineral.[2]

Chemical Laboratory
University of Missouri

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[1] Proc. Col. Sci. Soc., **8**, 1 (1905).

[2] Cf. Schlundt: "Radium in Some Tufa at Hot Springs, Arkansas," Trans. Am. Electrochem. Soc., **12**, 247 (1907).

EQUILIBRIUM IN THE SYSTEM: MERCURIC IODIDE AND ANILINE

BY J. N. PEARCE AND E. J. FRY

Those who have worked with aniline have no doubt observed its extraordinary high solvent power upon many of the inorganic salts. Like ammonia it also has the power of combining with the salts to form stable crystalline compounds containing from one to as high as six molecules of aniline of crystallization.

Among the large number of these crystalline compounds which have been prepared are $CoCl_2.2C_6H_7N$, $NiCl_2.2C_6H_7N$,[1] $Cu_2Cl_2.2C_6H_7N$, $Cu_2Br_2.2C_6H_7N$, $Cu_2I_2.2C_6H_7N$.[2] Tombeck[3] prepared the corresponding compounds of the chlorides, bromides, iodides and nitrates of zinc and cadmium and of magnesium nitrate. He also prepared similar compounds of zinc, cadmium, magnesium, nickel, cobalt and copper sulphates, all of which combine with two molecules of aniline except nickel sulphate which crystallizes with six molecules and cobalt sulphate which crystallizes with four molecules of aniline. Grossman and Hunter[4] prepared the compounds of the thiocyanates of cadmium, cobalt, nickel, iron, manganese and zinc, each combining with two molecules of the base. The dichromates of cobalt, nickel, copper, cadmium, zinc and manganese, each with four molecules of aniline were made by Parravaus and Pasta.[5] Françoise[6] contributed the compounds with the mercuric halides, each with two molecules of aniline of crystallization.

The usual method of preparing these compounds has been to treat alcoholic solutions of the salt with aniline, or *vice versa*.

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[1] Lippmann and Vortmann: Ber. chem. Ges. Berlin, **12**, 79 (1889).

[2] Saglier: Comptes rendus, **106**, 1422.

[3] Ibid., **124**, 961; **126**, 967.

[4] Zeit. anorg. Chem., **46**, 361 (1903).

[5] Gazz. chim. Ital., **37** II, 252 (1907).

[6] Jour. pharm. Chem., **6**, 21 (1906).

Only one system containing aniline and an inorganic salt has been studied quantitatively. This was done by Menschutkin[1] for the system: magnesium bromide and aniline. These two substances react with the liberation of much heat and produce three compounds. The temperature-solubility equilibrium curve consists of three parts, *viz.*, $MgBr_2.6C_6H_7N$ in equilibrium with its saturated solution at all temperatures up to 103°; that of $MgBr_2.4C_6H_7N$ between 103° and 237°; and probably the compound $MgBr_2.2C_6H_7N$ or $MgBr_2.C_6H_7N$ at still higher temperatures. Owing to the decomposition of the aniline the investigation could not be carried higher than 250°.

Owing to the relatively high solubility of mercuric iodide in aniline at ordinary temperatures, the dimorphic nature of the solid iodide and the power of the two to form stable crystalline compounds, it was thought worth while to make a careful study of this system over the maximum possible range of temperature. For this purpose the ordinary solubility method has been used.

Kahlbaum's aniline "I" was allowed to stand over fused potassium hydroxide for two weeks, then decanted and carefully distilled. Only that fraction passing over at 180°-182° was collected for the work, the first and last portions being rejected.

The mercuric iodide was precipitated from a saturated solution of chemically pure mercuric chloride by means of an equivalent weight of pure potassium iodide. The precipitate was allowed to settle and then washed by decantation, using large volumes of distilled water, until all traces of chlorine were removed. It was then transferred to a large Büchner funnel, washed with distilled water, sucked dry and finally spread upon porous plates and thoroughly dried.

The solubility measurements were made in an apparatus similar to the one used by Pearce and Moore.[2]

[1] Gazz. chim. Ital., **37**, I, 252 (1907).

[2] Am. Chem. Jour., **50**, 220 (1913).

For all temperatures between 0° and 42.9° an electrically heated and electrically controlled water thermostat was used; a cooling coil for running water was added for temperatures below that of the room. In this way temperatures constant to within ±0.02° could be maintained for any desired period of time. For temperatures above 42.9° the saturation tube was immersed in the vapor of a boiling liquid whose boiling point was approximately equal to the temperature desired. The tube containing the motor-driven spiral was inserted through a tightly fitting cork into a larger boiling vessel to the side tubule of which was fitted a long vertical condenser to prevent the loss of the boiling liquid by evaporation. The liquid was maintained at the boiling temperature by means of an electrically heated platinum spiral. In order to prevent variation in temperature due to radiation, which increases with the temperature, the whole apparatus, excepting the condenser, was inclosed in an asbestos case fitted with a glass door through which the temperature readings could be taken. In order to still further prevent the loss of heat by radiation, the inside of the case was heated by means of incandescent lights. By this means even the highest temperatures could be kept constant to within ±0.05°, any variation being due to changes in barometric pressure only.

For temperatures below 0° the saturation tube and stirrer were transferred to a larger tube which was surrounded by a freezing mixture of ice and salt. All temperatures were read on a certified thermometer passing through the cork and kept at the same level as the material in the saturation tube. The thermometers were graduated in 0.10° which easily permitted estimations accurate to ±0.05°.

Repeated tests showed that saturation was complete in about one and one-half hours. In most cases, however, the time allowed for saturation was much longer, except at the three highest temperatures where, owing to decomposition, the time had to be limited.

After saturation was complete the stirrer was stopped, the solid phase allowed to settle and a sample of the liquid phase was removed by means of a small tube covered at one end by a double thickness of thin muslin. In order to prevent solidification within the tube the latter was heated to a temperature slightly higher than that of the saturated solution. All samples were run at once into dry glass-stoppered weighing bottles and kept in dry desiccators until analyzed.

The difficulties in the analysis of either phase of the system are readily appreciated when one considers the volatile nature of the iodide and its inertness toward ordinary reagents. The complications are still further increased by the difficulty in eliminating the easily oxidized aniline and its oxidation products.

Obviously the simplest method would be to remove the aniline by means of organic solvents and weigh the iodide directly, but this is impossible on account of the appreciable solubility of the mercuric iodide in these solvents. An attempt was made to dissolve out the aniline with dilute hydrochloric acid, but here also the iodide was found to be appreciably soluble in the aniline hydrochloride formed. Likewise the electrolytic method was found to be unsatisfactory because of the formation of aniline black at the anode. This was deposited upon the surface of the mercury and the exposed platinum and could not be removed.

The method finally adopted was to dissolve the sample in a solution of acetic acid containing an excess of potassium iodide and to precipitate the mercury as the sulphide by passing in hydrogen sulphide to complete precipitation. This method proved to be very satisfactory and was used in all determinations.

Samples taken at the three highest temperatures seemed to be more difficultly soluble and complete transformation to the sulphide was accomplished by placing the solid mass in the acetic acid-potassium iodide solution and passing hydrogen sulphide for two or three hours until portions of the filtrate gave no test for mercury on further treatment with hydrogen sulphide. The precipitate was then transferred to a weighed Gooch crucible, washed with water and absolute alcohol and then gently dried. The free sulphur was removed by carbon bisulphide in an electrically heated extraction apparatus of the form recommended by Treadwell and Hall.[1]

The quantities of acetic acid or potassium iodide added did not seem to affect the speed of transformation of the iodide to the sulphide, but the physical nature of the precipitate was considerably improved, if the system was heated slightly before filtration.

The sulphur-free precipitate was then placed in an air bath and heated to 110°, the temperature recommended by Treadwell and Hall. The weights obtained after successive heatings were found to decrease constantly with the time of heating. Believing that this inconstancy is due to the volatilization of the sulphide, experiments were made to test the effect of temperature upon the extent of volatilization of the sulphide. Weighed Gooch crucibles containing the pure dry sulphides were heated for intervals of one to three hours at 70°, 80° and 110°. The results are recorded in Table I.

TABLE I

HgS Grams	One hour at 110°	Two hours at 110°
1.4352	1.4202	1.2784
2.3076	2.2321	2.0375
	Two hours at 80°	Three hours at 80°
0.5412	0.5378	0.5300
0.6879	0.6765	0.6685
	One hour at 70°	Three hours at 70°
0.4311	0.4311	0.4311
0.4432	0.4432	0.4431
0.2054	0.2054	0.2054
0.1802	0.1801	0.1801

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[1] "Analytical Chemistry," Vol. II, third edition, p. 169.

All the data in the following tables were obtained by heating the precipitates to constant weight at 70°. By observing these precautions results were obtained which leave little to be desired as to the accuracy of the method. Analyses made on known weights of mercuric iodide in aniline gave the following results:

TABLE II

Grams taken	Grams found
0.4325	0.4323
0.2936	0.2930
0.5872	0.5872

The results of the solubility determinations made in this work are given in Table III and they are graphically represented by the Curve, Fig. 1.

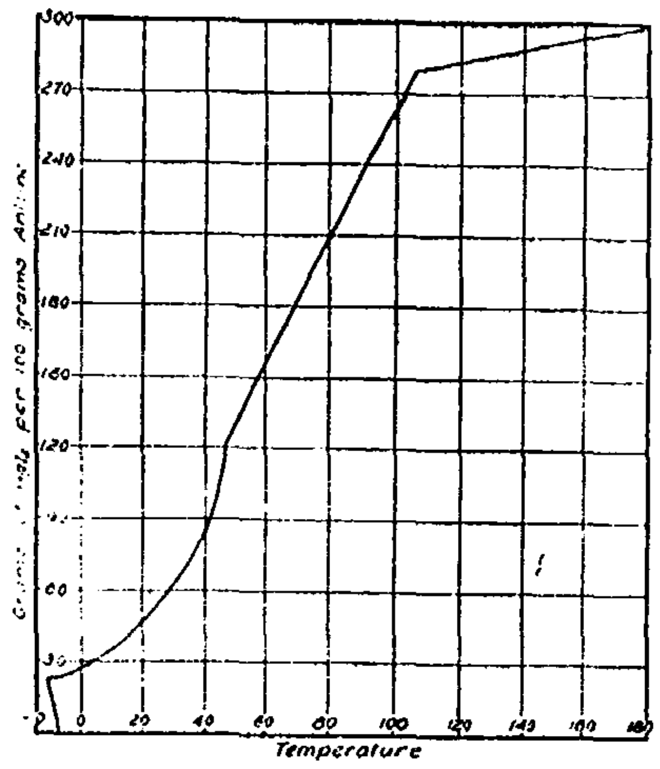

Fig. 1

The freezing point of aniline, purified according to the method of Hantzsch, was found by one of us[1] to be −8° C,

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[1] Pearce.

TABLE III

Temp.	Solution phase Grams	HgS	HgI$_2$.	Gr. HgI$_2$ per 100 gr. of aniline	Mean
—6.5°	4.0110	0.3910	0.7636	23.52	23.35
—6.5	3.7128	0.3667	0.7162	23.10	
—6.5	3.8273	0.3719	0.7264	23.42	
+0.4	1.3666	0.2054	0.4012	28.72	28.69
0.4	2.8167	0.3214	0.6277	28.68	
0.4	1.5798	0.1802	0.3519	28.66	
17.8	2.8032	0.4311	0.8420	42.94	42.85
17.8	2.8818	0.4432	0.8670	42.80	
17.8	2.8667	0.4396	0.8586	42.81	
21.10	3.0095	0.4937	0.9867	47.43	47.55
21.1	2.7408	0.4543	0.8848	47.67	
26.9	3.7408	0.6842	1.3365	55.58	55.47
26.9	2.7353	0.4987	0.9707	55.35	
30.1	3.5303	0.6927	1.3530	62.14	62.05
30.1	3.3077	0.6478	1.2650	61.96	
36.2	2.4979	0.5512	1.0770	75.76	75.80
36.2	2.9044	0.6456	1.2610	76.03	
36.2	3.1347	0.6879	1.3435	75.72	
42.9	3.2802	0.8204	1.6025	96.60	96.49
42.9	3.4225	0.8604	1.6805	96.47	
42.9	3.5057	0.8812	1.7210	96.40	
48.8	3.6347	1.0447	2.0480	128.4	128.1
48.8	3.6440	1.0509	2.0530	128.0	
48.8	3.8001	1.0901	2.1290	127.9	
63.6	2.4242	0.7680	1.5000	162.9	163.8
63.6	2.0912	0.6652	1.2990	164.0	
63.6	2.1322	0.6833	1.3350	163.6	
70.82	7.4980	2.4870	4.8580	184.0	184.1
70.82	7.4982	2.4890	4.8600	184.2	
76.2	4.3407	1.4910	2.9120	202.5	201.6
76.2	3.6806	1.2586	2.4590	201.2	
95.9	1.5092	0.5500	1.074	246.8	246.7
95.9	1.5092	0.5497	1.072	246.5	
115.7	2.2309	0.8456	1.6520	281.8	281.8
115.7	1.3955	0.5274	1.0300	281.8	
137.2	0.6997	0.2648	0.5172	284.9	285.2
137.2	0.1893	0.0720	0.1490	286.5	
181.1	0.9820	0.3763	0.7350	297.6	297.9
181.1	2.4612	0.9823	1.9180	298.3	
199.1[1]	2.1435	0.9797	1.9140	862.5	863.2
199.1	0.7405	0.3384	0.6644	864.0	

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[1] Not plotted.

a value identical with that found by Lucius.[1] That part of the curve between —8° and —11.48° represents the freezing point curve for the solution in equilibrium with solid aniline.

At —11.48° solid aniline and the compound $HgI_2.2C_6H_7N$ separate out together in the form of a eutectic mixture. This point was determined three times by plotting the cooling curve of the saturated solution. In a freezing point tube fitted with a thermometer and stirrer and surrounded by an air jacket was placed the saturated solution. The whole was placed in a freezing mixture of ice and salt (—16°) and gently stirred until a slight undercooling was obtained. The temperature then quickly rose to the eutectic point where it remained constant until the entire mass had solidified and then fell slowly to the temperature of the bath. The points obtained were —11.5°, —11.55° and —11.4°, the mean being —11.483°.

Beginning with the eutectic point the solubility of the mercuric iodide increases gradually up to about 10° and then at a more rapidly increasing rate up to 46.8°. The white crystalline solid in equilibrium with the saturated solution has the composition $HgI_2.2C_6H_7N$. Its melting point is 58.6°. These crystals have parallel cleavage and parallel extinction; they belong to the third or fourth system, but it was impossible to determine exactly which.

At 46.8° we have a quadruple point representing an equilibrium between the two solids, HgI_2, $HgI_2.2C_6H_7N$, the saturated solution and aniline vapor.

From this point on the solubility curve rises rapidly and linearly with rise in temperature up to 108°, the solid phase in equilibrium being the red mercuric iodide. At 108° we have a second quadruple point, the solids being the red and yellow mercuric iodides in equilibrium with the saturated solution and vapor. The transition point between the red and the yellow iodides is apparently lowered by the influence of the solvent from 126° to 108°. This is in accord with the

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[1] Ber. chem. Ges. Berlin, 5, 154 (1872).

work done by Kastle[1] in which he finds that the transition point of the iodide is affected by the solvent used.

An insoluble greenish yellow solid begins to appear at about this temperature and the solution assumes a violet permanganate color.

Above 108° the solubility of the yellow iodide increases but slightly up to approximately 200°. Beyond this point the highly viscous liquid phase seemed to be in equilibrium with the solid yellow mercuric iodide. The entire mass solidified to a pasty solid on cooling which on standing gradually passed over into the crystalline form. On account of the rapid decomposition of the components at these high temperatures further measurements were entirely out of question.

The insoluble solid coming in at 108° and above was isolated, thoroughly washed with acidulated water and alcohol. It is a greenish yellow, flaky, mica-like solid belonging to the fifth or sixth system. It is insoluble in water, alcohol, hot aniline, or the ordinary acids, but dissolves with decomposition in potassium cyanide, liberating free mercury. Its analysis was difficult. Small weighed samples of the clean solid were placed in a weighed platinum dish and the mercury determined electrolytically. Weighed quantities of the solid were also added to strongly acidified solutions of silver nitrate, the suspension was heated and then allowed to stand until transformation was complete. From the weights of the silver iodide precipitated the approximate percent of iodine was calculated. The percentages of mercury and iodine found correspond approximately with the values calculated for the undescribed compound, $C_6H_7N.Hg_2I_2$, *e. g.*,

	Found Percent	Calculated Percent
Hg	56.9	53.77
I	35.7	34.02

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[1] Am. Chem. Jour., 22, 473 (1899).

Summary

The system of mercuric iodide and aniline has been studied for temperatures between $-11.48°$ and $181°$ and the curve representing the conditions of equilibrium has been plotted.

The region of stability of the three solids, $HgI_2.2C_6H_7N$, red HgI_2 and yellow HgI_2, in the presence of aniline has been established.

A new compound corresponding to the formula $C_6H_7N.Hg_2I_2$ has been identified and described.

A method for the determination of mercuric iodide in the presence of an easily oxidized organic solvent has been tested and applied.

Physical Chemistry Laboratory
The State University of Iowa

THE THERMAL EXPANSION OF SOLUTIONS OF GELATINE IN WATER

BY ARTHUR A. SCOTT

Colloid chemistry, that comparatively new branch of chemical science, has to deal in general with two types of colloidal solutions; hydrosols, which closely resemble ordinary liquid solutions, and hydrogels, which possess a gelatinous constituency. Into the latter classification fall those solutions of gelatine in water, commonly known as jellies. Their chemical behavior has been extensively studied in all branches of the science, but comparatively little is known concerning their physical properties.[1] Rubber, as a typical colloid, however, is known to have a negative coefficient of thermal expansion. It is possible by observing the thermal expansion of jellies to learn how the expansion changes with the concentration, from pure water to pure gelatine. The present paper gives an account of the study of the expansion of 2 percent, 6 percent and 10 percent solutions of gelatine in water, between 0° and 10° C.

The apparatus with which the experiments were carried out is shown in Fig. 1. A helix of glass tubing of constant

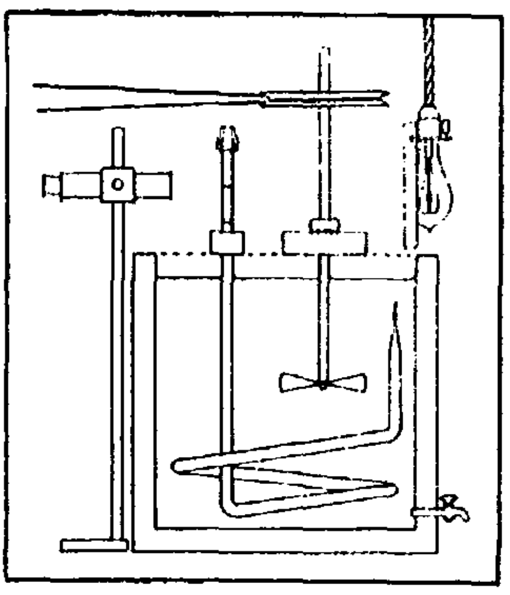

Fig. 1—Thermostat for measuring the thermal expansion of gelatine solutions

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[1] Compare P. von Bjerkén: Wied. Ann., 43, 817 (1891).

cross-section, 150 cm long, drawn down at one end to capillary size, contained the solution under examination. A small amount of bichloride of mercury was first dissolved in the water of solution to destroy any bacteria which would otherwise melt the jelly. Gelatine was then dissolved in the water when heated. The tube was filled to a certain mark with the hot solution, and the capillary end sealed in a flame. It was impossible to employ the meniscus of the jelly as a criterion of expansion, as it adhered to the glass at the edge and also developed cracks. One centimeter of kerosene oil was placed above it and the oil meniscus was observed. This proved satisfactory, for, since oil wets glass, its meniscus preserves a constant shape, and also its evaporation is small. To prevent it from creeping over the edge of the tube and flowing down the outside, a small piece of rubber tubing was placed on the open end.

The glass tube was held in a fixed position in a jacketed water bath. By introducing ice, the temperature could be maintained at any point between room temperature and zero, and could be read by a thermometer to one-tenth of a degree. The water was kept constantly stirred by a paddle, so that any change in temperature almost immediately affected the entire bath. The oil meniscus was observed through a microscope which read to 0.008 cm, tenths of which could be estimated.

The true expansion of each solution was obtained in the manner described in Preston's "Theory of Heat." The tube was filled with water and the apparent expansion of the water observed. The difference between the true expansion, which is known, and the apparent expansion was plotted on a temperature base. The slope of a straight line through the points represented the coefficient of cubical expansion of the glass. In this experiment it was 0.000025. The apparent expansion of each solution was then plotted against the temperature. From the origin, a straight line was drawn with a negative slope equal to that of the first line. The vertical distance between the curve and the line at any point on the temperature axis measured the true expansion at that temperature. These differences, expressed as millionths of the volume at zero, are tabulated below and are shown graphically in Fig. 2.

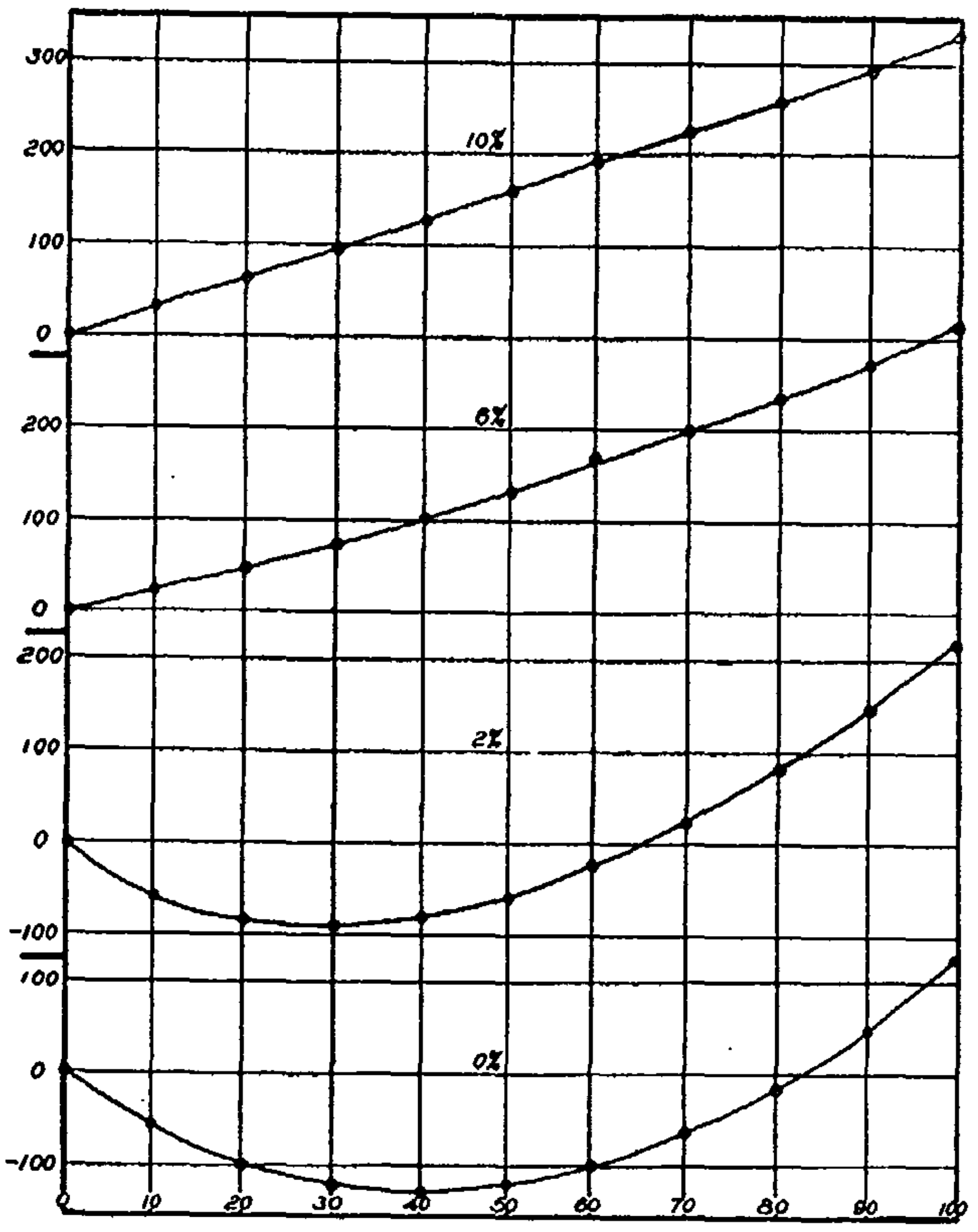

Fig. 2—Thermal expansion of gelatine solutions

TABLE OF THERMAL EXPANSION OF GELATINE SOLUTIONS

Expansion (× 10^6)

Temp.	Water (True)	2 percent	6 percent	10 percent
0	0	0	0	0
1	— 57	—60	20	30
2	— 98	—85	45	60
3	—120	—90	70	95
4	—129	—80	100	125
5	—119	—60	130	160
6	— 99	—25	170	190
7	— 62	25	200	225
8	— 15	80	235	255
9	47	145	270	290
10	124	215	315	330

It is hoped to continue the observations for solutions of higher concentration as soon as time will permit.

Macdonald Physics Building
McGill University
June 26, 1914

THE DISTRIBUTION OF COLLOIDAL ARSENIOUS SULPHIDE BETWEEN THE TWO LIQUID PHASES IN THE SYSTEM WATER, ETHER, ALCOHOL

BY HARRY P. CORLISS

The present paper gives the results of some quantitative measurements of the distribution of colloidal arsenic trisulphide between the two liquid phases formed when ether, water and alcohol are mixed in proper proportions; that equilibrium involving the distribution of colloids may be realized experimentally was established in 1908 by Lash Miller and McPherson,[1] who made also a preliminary study of the conditions affecting the distribution ratio.

The binodal curve and the tie lines at 0° C for the system Ether—water—alcohol were determined by Bonner,[2] who employed a method designed rather to permit measurement with very small quantities than to furnish extremely accurate results. As a preliminary, therefore, it was necessary to redetermine the curve and lines; accurate specific gravity measurements also were made of solutions of known composition on the binodal curve, and a graph was constructed so that the composition of any one of a pair of solutions in equilibrium could be found simply by determining its density.

Satisfactory methods of preparing the colloidal solutions and of determining their content of arsenic were then worked out, and a method of allowing for the effect of the colloid on the specific gravity of the solutions was checked experimentally. Finally, some twenty measurements of the distribution ratio were made and their results collated.

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[1] Jour. Phys. Chem., 12, 709 (1908); see also Reinders: Zeit. Kolloid-Chemie, 13, 235 (1913).

[2] Jour. Phys. Chem., 14, 738 (1910); a very complete study of the system alcohol-water-ether at 25° C has been made by Shinkichi Horiba, see Memoirs of the College of Science and Engineering, Kyoto Imperial University, Vol. 3, No. 3, p. 63 (1911).

Binodal Curve, Tie-lines, Specific Gravities

In determining the points of the binodal curve, and in all other experiments of this paper, Kahlbaum's ether "über Natrium destilliert," and Kahlbaum's "ethyl alcohol 99.8 percent" were used; account was taken of the water added with the alcohol; the total weight of the liquids used in each determination of a point on the binodal curve was about 25 grams.

The liquids were weighed into the mixing tube from pycnometers of the Ostwald-Sprengel type, provided with a long fine exit-tube, suitably bent. The tube in which the liquids were mixed was about 10 cm long and 2.5 cm in diameter. Into the mouth was fitted tightly a cork through which passed a short glass tube of about 1 cm diameter, and over the end of this tube two overlapping pieces of thin sheet rubber were drawn and tied. This allowed the end of a pycnometer to be inserted with the least loss of vapor; and while containing the liquids and immersed in ice water, no smell of alcohol or ether could be detected, showing that the sheet rubber was an effective means of closing the tube.

A point on the binodal curve was determined by blowing over from the pycnometers into the tube the desired amounts of ether and water; then adding alcohol in quantity nearly but not quite enough to make all homogeneous, the tube being all the time immersed in ice water to keep the vapor tension as low as possible. The tube was then removed to an ice bath provided with a stirrer run by a small motor, and allowed to cool for about fifteen minutes more, being frequently stirred by giving the liquid in the tube a rotating motion. Then a little more alcohol was added from the pycnometer, mixed well by rotating and gently shaking, and placed again in the ice bath to see if it would separate into layers. The final addition of alcohol was made easy, however, without waiting long for separation to occur, by the fact that even when a long time would be required for separation to take place, a silky appearance of the liquid, when shaken, was seen; and then the alcohol was added, drop by drop, until the last drop just caused this silky appearance to disappear. That this method of judging the final addition of alcohol was accurate, was tested many times; whenever a silky appearance was noted, separation always occurred on standing in the bath, and no separation occurred after just enough alcohol had been added to dissipate this silky appearance on shaking. Of course, when points on the binodal curve where the two layers were of widely different specific gravities were being found, separation took place more rapidly than near the top of the curve, so that actual separation was obtained quickly; in such cases the diminishing amounts of either upper or lower phase served to indicate how much more alcohol should be added to make homogeneous. After the liquid was made homogeneous the specific gravity was taken. Such an experiment gave the composition and specific gravity for one point in the binodal curve.

The results of these measurements are given in Table I and Fig. I, in which the weights of ether and water taken

TABLE I—EXPERIMENTAL DATA FOR BINODAL CURVE
Temperature 0° C Specific Gravity of Water at 0° C 1.0000

Ether	Water	Alcohol	Specific gravity
0.128	0.872	0.237	0.9619
0.199	0.801	0.338	0.9397
0.291	0.709	0.365	0.9175
0.295	0.705	0.369	0.9160
0.345	0.655	0.375	0.9044
0.390	0.610	0.378	0.8939
0.446	0.554	0.388	0.8822
0.506	0.494	0.383	0.8698
0.549	0.451	0.385	0.8600
0.597	0.403	0.377	0.8500
0.649	0.351	0.361	0.8383
0.724	0.276	0.343	0.8227
0.817	0.183	0.301	0.8017
0.873	0.127	0.278	0.7878
0.915	0.085	0.207	0.7734
0.958	0.042	0.135	0.7575
0.488[1]	0.512	0.385	0.8738

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[1] Plait point obtained by graphic interpolation from tie-line graph and binodal curve.

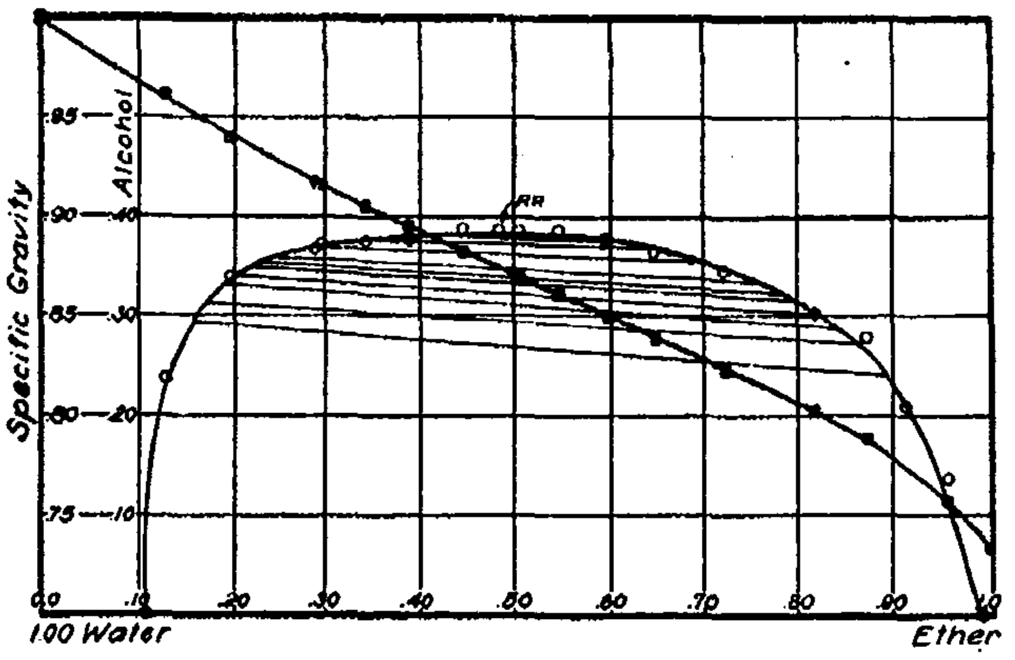

Fig. I—Binodal curve and tie-lines

together amount to one gram; the weight of alcohol given is therefore the amount needed to make one gram of the ether-water mixture homogeneous. The data of Table II were obtained by graphic interpolation from Table I; the last two

TABLE II—INTERPOLATED VALUES FOR BINODAL CURVE

Ether e	Water w	Alcohol a	Log $\frac{w}{a}$	Log $\frac{e}{a}$
0.980	0.020	0.035	$\bar{1}$.757	1.447
0.975	0.025	0.060	$\bar{1}$.620	1.211
0.950	0.050	0.145	$\bar{1}$.538	0.816
0.900	0.100	0.240	$\bar{1}$.620	0.574
0.850	0.150	0.290	$\bar{1}$.714	0.467
0.800	0.200	0.315	$\bar{1}$.803	0.405
0.750	0.250	0.335	$\bar{1}$.873	0.350
0.700	0.300	0.351	$\bar{1}$.932	0.300
0.650	0.350	0.365	$\bar{1}$.982	0.251
0.600	0.400	0.376	0.027	0.203
0.550	0.450	0.384	0.069	0.156
0.500	0.500	0.385	0.114	0.114
0.450	0.550	0.384	0.156	0.069
0.400	0.600	0.382	0.196	0.020
0.350	0.650	0.377	0.237	$\bar{1}$.968
0.300	0.700	0.371	0.276	$\bar{1}$.908
0.250	0.750	0.360	0.319	$\bar{1}$.842
0.200	0.800	0.339	0.373	$\bar{1}$.771
0.150	0.850	0.281	0.481	$\bar{1}$.727

columns give the "logarithmic coördinates" of Bancroft's formula,[1] plotted in Fig. II.

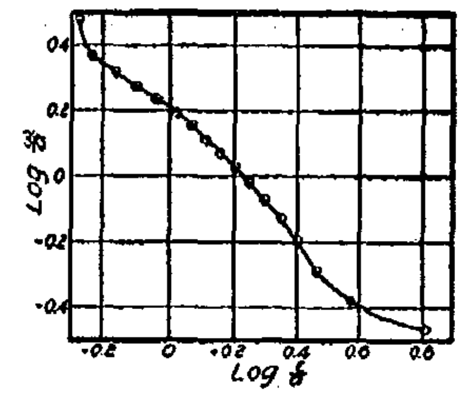

Fig. II—Binodal curve (logarithmic coördinates)

Specific Gravities.—For the purpose of taking specific gravities the left-hand pan-rest was removed from a Sartorius analytical balance which had pan-rests that rose through a hole in the base. To the bottom of the pan a hook was cemented and from it hung a platinum wire extending through the base and shelf on which the balance sat. Below the balance shelf a cork of the size to fit the mixing tube was rigidly clamped, and through it a small glass tube was fitted. From the platinum wire a human hair extended through the glass tube in the cork to a distance below sufficient to have the bulb, whose loss in weight was measured, hang immersed in the liquid when the tube was placed on the stopper. The bulb was made of glass of about 4 cc volume, partially filled with mercury, and was suspended by a small platinum hook fastened to the end of the hair. The hair suspension proved very satisfactory; fine tungsten wire was also tried. In making a specific gravity determination, the tube containing the liquid was removed from the ice bath and placed quickly on the stopper below the balance; the ice bath was then raised, so that the liquid would be kept at 0° C in the new position. After a few minutes,[2] to allow the liquid to cool completely again, the weight of the bulb, immersed in the liquid, was taken. From the loss in weight in the liquid and the loss in

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[1] See Bonner: Jour. Phys. Chem., 14, 738 (1910).

[2] The mixing tube and its contents left in the ice bath, with frequent stirring, fell from 18° C to 0.1° C in five minutes.

water, the specific gravity was calculated; the results of the measurements are given in Table I and Fig. I.

Tie-lines.—For the determination of the tie-lines, ether water and alcohol were mixed in the proportion to give a tie-line at the approximate position desired, about 100 grams in all being taken for each experiment. This mixture was allowed to cool and separate into layers in the ice bath; a portion of each layer was siphoned off by a glass tube and its specific gravity taken; and, from the specific gravity and binodal curves, the composition of the phases at the end of the tie-line was determined. Since the loss of weight in water was about four grams for the specific gravity bulb used, and this loss could be determined within 0.2 mg, the specific gravities could easily be determined to four decimal places; the composition of the solutions of the binodal curve, of course, are not known with any such accuracy. The results are given in Table III and in Fig. III. The composition of the solution at the plait point was ascertained by prolonging the curve of Fig. III, and choosing the point on the extrapolated curve whose ordinate was equal to its abscissa; the result is in good agreement with that obtained by interpolation in Fig. I.

TABLE III—EXPERIMENTAL DATA FOR TIE-LINES
(Specific gravities at 0° C referred to water at 0° C as 1.0000)

	Upper layer	Lower layer
(1)	0.7400	0.9826
(2)	0.7787	0.9505
(3)	0.7880	0.9452
(4)	0.7939	0.9412
(5)	0.8000	0.9371
(6)	0.8081	0.9322
(7)	0.8102	0.9296
(8)	0.8149	0.9262
(9)	0.8273	0.9162
(10)	0.8385	0.9057
(11)	0.8574	0.886
(12)	0.8738[1]	0.8738

[1] Plait point.

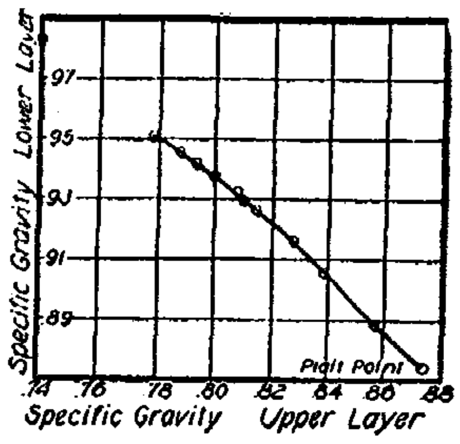

Fig. III—Tie-line plot

The Colloidal Solutions

A solution of arsenious acid was prepared by boiling water to remove air, adding about one gram arsenious oxide per hundred grams of water and boiling slowly until all was dissolved. The solution was then cooled, an equal volume of alcohol was added, and hydrogen sulphide was passed in to excess. The whole was then allowed to stand some hours, usually over night, and then hydrogen[1] was bubbled through until paper moistened with silver nitrate and held over the mouth of the tube was no longer blackened. Both gases were washed by passing through two wash bottles of water.

The colloidal arsenious sulphide prepared in solutions containing alcohol or ether or both was much clearer than when water alone was used; if ether was present, however, the solution on standing underwent some change, the effect of which was that, on coagulating with acid and filtering, the filtrate contained considerable amounts of arsenic. If only water and alcohol were present, the amount of arsenic present in the filtrate after coagulation was small, and was constant for a given preparation. The change in the ether solutions was probably due to oxidation induced by the ether.[2]

Removal of Hydrogen Sulphide by Lead Carbonate.—If a colloidal solution of arsenious sulphide containing alcohol

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[1] Picton: Jour. Chem. Soc., 61, 137 (1892).

[2] Argo: Trans. Roy. Soc. Canada, 1913, Sec. III.

and excess hydrogen sulphide be cooled in ice water, shaken with lead carbonate, and quickly filtered, using a funnel jacketed with ice, the excess of hydrogen sulphide is removed, and after coagulation but a small amount of arsenic is found in the filtrate. Quick work is necessary, however, as on prolonged shaking with lead carbonate the liquid is completely decolorized and the filtrate after coagulation contains arsenic; if a solution containing no free hydrogen sulphide is used, the lead salt is colored salmon to brown, if hydrogen sulphide be present, black.

Coagulation.—The sulphide is not so easily coagulated in solutions containing ether and alcohol as in pure aqueous solutions. Hydrogen sulphide in excess was passed into a solution made up from 35 cc one-percent arsenious oxide, 25 cc alcohol, and 20 cc ether. To 3 cc of this were added 5 cc alcohol and 5 cc water, and then a measured amount of salt solution; the mixture was let stand 5 minutes and was compared in reflected light with a sample to which no salt had been added. If no turbidity was observable, the experiment was repeated, using more of the salt solution, and so on until a slight turbidity was noticed. The following results were obtained:

Turbidity produced by
0.08 cc alum solution, containing 0.01 gram-mols[1] per liter
0.40 cc barium chloride solution, 0.01 gram-mols per liter
0.50 cc hydrochloric acid, 0.01 gram-mols per liter

Alum is thus the best coagulant of the three, and hydrochloric acid the worst, the same as in aqueous solutions; but there is not nearly as much difference as in the latter case, the ratios being 1 : 5 : 6.3, while Linder and Picton[2] found the ratios 1 : 32 : 1590 for aqueous solutions.

Determination of Arsenic.—The arsenic was estimated in solutions containing sulphide, ether, alcohol and water, by evaporating to dryness in a beaker on a water bath, after co-

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[1] $KAl(SO_4)_2.12H_2O$.

[2] Jour. Chem. Soc., 67, 65 (1895).

agulating with a drop of sulphuric acid. About 15 cc of concentrated sulphuric acid was then added and the whole heated on a gauze for some time after dense white fumes began to come off, or until the solution became quite clear and all free sulphur had disappeared; the sulphur dioxide formed keeps the arsenic reduced as arsenious acid. It was then cooled, diluted, nearly neutralized with ammonia, and then made alkaline with a saturated solution of ammonium or sodium bicarbonate, using about 10 cc in excess of that necessary for neutralization. The solution was then cooled in ice water and titrated with tenth or hundredth normal iodine according to the amount of arsenic present. The volume of final solution titrated was usually about 300 cc; starch was used as indicator and a small crystal of potassium iodide was added.

Determination of Hydrogen Sulphide.—In connection with this work a convenient method of determining the strength of an aqueous solution of hydrogen sulphide was worked out. A known volume of the solution was run into a measured excess of volumetric silver nitrate; a little precipitated calcium carbonate free from chlorides was then added, and the whole boiled and filtered. The excess of silver in the solution was then determined volumetrically by sodium chloride with potassium chromate as indicator. This method was found to be more reliable than oxidation with iodine.

Effect of As_2S_3 on the Binodal Curve.—It seemed very improbable that the presence of the colloidal sulphide could affect the composition of the solutions of the binodal curve; but, to make sure, a direct determination was made, as described on page 682, using in place of water an aqueous solution containing 11.7 g arsenious sulphide per liter, and subtracting the weight of colloid to obtain the weight of water used. The result (expressed as in Table I) was:

Ether 0.494 Water 0.506 Alcohol 0.385 Sp. gr. 0.8748

giving a point that fits right on the curve obtained in absence of arsenic.

Effect of As_2S_3 on the Specific Gravity.—One cubic centimeter of the solution of the preceding paragraph thus weighs 0.8748 gram and contains

$$0.8748 \times 0.0117 \times 0.506/1.1385 = 0.0037 \text{ g. } As_2S_3$$

The specific gravity of amorphous arsenious sulphide is 2.76;[1] assuming that of the suspended sulphide to be the same, the volume of the 0.0037 gram would be 0.0014 cc, and the remaining 0.8748 — 0.0047 = 0.8711 gram of liquid would occupy 1.0000 — 0.0014 = 0.9866 cc, corresponding to a specific gravity of 0.8723 which agrees well with the interpolated specific gravity 0.8724 of the arsenic free solution of the binodal curve.

As a further check, a "tie-line determination" was made, the arsenic content and the specific gravity of upper and lower layers being determined. The gravities were then corrected for the arsenious sulphide present, and the "corrected" values were found to lie on the line in Fig. III. The numbers found were:

Upper layer 0.0007 g As_2S_3 per cc, Sp. gr. 0.8612 corr. 0.8608
Lower layer 0.0074 As_2S_3 per cc, Sp. gr. 0.8904 corr. 0.8855

Distribution Experiments

Measured amounts of the aqueous-alcoholic colloidal solution of arsenious trisulphide were brought into a cylindrical glass stoppered 200 cc bottle, about 13 cm tall; enough alcohol, water and ether were then added to nearly fill the bottle with a two phase liquid system of the desired composition. The whole was kept in the ice bath, and when the lower layer had settled a little, leaving the upper layer transparent, the amount of sulphide in the latter could be roughly estimated by the color. Very small amounts of the reagents, sometimes but one or two drops, were then added, until after shaking and letting stand the upper layer showed the color desired.

After complete separation of the phases had taken place, about 25 cc of the upper layer was siphoned off and its specific

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[1] Hausmann: Liebig's Ann., 74, 199 (1850).

gravity taken. Two other portions of the upper and lower layers, usually 25 cc of upper and 10 cc of lower layer, were withdrawn for estimation of total arsenic; and still another portion of each layer was coagulated with a drop of sulphuric acid, filtered, and the arsenic in the filtrate determined. The difference between "total arsenic" and "arsenic in filtrate" gives arsenic as arsenious sulphide.

The first determinations (Colloids I and II) were made from small amounts of freshly prepared colloidal solutions; but as they showed that different colloidal solutions may give different ratios of distribution for the same composition of the phases (as regards ether, water and alcohol) a stock of colloidal solution (Colloid III) was prepared from 400 cc of 1 percent aqueous solution of arsenious oxide and an equal volume of alcohol as described on page 687, and was used in experiments (5) to (13); colloids IV and V were likewise made up in quantity.

The results of the measurements are given in Table IV; the composition of the upper layer is recorded by the method of Table I; in expt. (1), for instance, for every 0.552 gram ether in the upper layer there was 0.448 gram water and enough alcohol to make up a solution of the binodal curve. Under As_2O_5 is given the result of the arsenic determination in the filtrate after coagulation, calculated as arsenic anhydride; and under As_2S_3 the difference between total arsenic and arsenic as As_2O_5, calculated as As_2S_3.

The data of Table IV are plotted in Fig. IV; the points joined by a curve were all made with one colloidal solution (Colloid III) and were made with the fewest number of additions of reagents to get distribution, and hence with least amount of shaking and in the shortest time; the average time in the ice bath being about three hours. Points 12 and 13 were made with Colloid III, which had stood in the presence of ether and alcohol for several days. When the layers separated quickly, indicating considerable difference in specific gravity, sometimes a little colloid would be seen in the upper layer; in such cases the upper layer had a milky appearance

TABLE IV—DISTRIBUTION DATA

		Upper layer			Lower layer		Ratio
	Ether	As_2S_3 per liter Gram	As_2O_5 per liter Gram		As_2S_3 per liter Grams	As_2O_5 per liter	Gms. As_2S_3 in L. L. / Gms. As_2S_3 in U. L.
			COLLOID I				
(1)	0.552	0.177	0.035	—	5.61	—	31.6
(2)	0.559	0.293	0.030	—	15.62	0.104	53.4
			COLLOID II				
(3)	0.536	0.875	0.046	—	4.86	0.046	5.56
(4)	0.547	0.764	0.030	—	7.32	0.058	9.58
			COLLOID III				
(5)	0.554	0.600	0.023	—	7.95	0.028	13.2
(6)	0.555	0.556	0.023	—	7.75	0.046	13.9
(7)	0.592	0.0861	0.021	—	9.55	—	111.0
(8)	0.571	0.0492	0.021	—	5.26	0.046	107.0
(9)	0.537	0.613	0.046	—	5.15	—	8.41
(10)	0.566	0.516	0.025	—	15.18	—	29.4
(11)	0.562	0.226	0.028	—	4.80	—	21.2
(12)	0.541	0.0674	0.023	—	2.19	—	32.5
(13)	0.541	0.0588	0.030	—	1.78	—	30.3
			COLLOID IV				
(14)	0.551	0.669	0.013	—	10.0	0.030	14.9
(15)	0.544	2.18	0.018	—	16.1	0.069	7.38
(16)	0.545	0.976	0.014	—	11.3	0.023	11.6
(17)	0.535	0.971	0.011	—	6.62	0.021	6.81
(18)	0.544	0.212	0.046	—	5.44	0.122	25.6
			COLLOID V				
				Time in ice bath			
(19)	0.562	0.283	0.025	3 hrs.	6.86	0.064	24.2
(20)	0.566	1.11	0.014	5 hrs.	20.6	0.104	18.5
(21)	0.567	0.223	0.012	4 hrs.	10.42	0.110	46.7
(22)	0.566	0.0258	0.025	7 hrs.	5.29	0.122	205.0

and was not clear as in the case of true distribution. Point 7 illustrates this condition.

In the experiments with Colloid IV it was planned to have the upper layer much more concentrated with respect to the colloid than in former determinations. The points do not lie on a smooth curve.

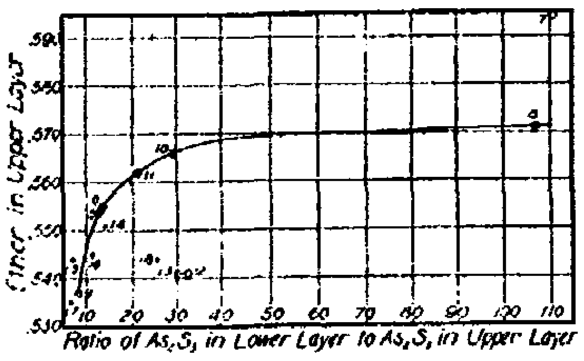

Fig. IV—Distribution plot: ⊙ colloid 3; + colloid 4

In Experiment 18, also with Colloid IV, the solutions were made up at the close of a day's work, and—to judge by the eye—the concentration of the colloid in the lower layer was about ten times as great as in the upper. The whole was then allowed to stand at room temperature over night, with the glass stopper firmly tied in to prevent loss of vapor. Next day, after cooling and shaking, it was at once apparent that the amount of colloid in the upper layer had greatly diminished; and on making the usual density determinations and analyses, a ratio was obtained which is much greater than fits in with the other experiments with the same colloid.

The measurements with Colloid V (19–22) were made with the object of obtaining phases of the same composition as regards ether, water and alcohol, but widely different in the concentration of the colloid. The method was to get the layers as nearly as possible of the right composition, and then to take the specific gravity of a portion of the upper layer, and, guessing at the correction for arsenious sulphide, obtain its composition from Fig. III. This portion was then replaced, a small amount of the proper liquid added in order to approach more nearly the desired density, and the whole was shaken and allowed to separate again. These operations were repeated until an upper layer of the desired density was obtained. Fair success was had in getting closely the same composition of phases as regards the organic liquids and water; but as seen in Table IV, the arsenic concentration ratios varied greatly.

Conclusions and Summary

Data have been obtained for the binodal curve and tie-lines in the system Alcohol-water-ether at 0° C; the densities of the phases at equilibrium have been determined; and a method of allowing for the effect of colloidally dissolved arsenious sulphide on these densities has been checked experimentally. As regards alcohol, water and ether, the compositions of the phases at equilibrium are not affected by the presence of colloidal arsenious sulphide.

Colloidal solutions of arsenious sulphide containing alcohol and ether are more transparent and are less readily coagulated by salts than aqueous solutions, and there is not so much difference between the amounts of different salts needed to coagulate them.

Solutions containing alcohol, water, ether, and arsenious sulphide undergo change on standing; the amount of arsenic found in the filtrate after coagulation with acid increases, and the proportion of colloid going into the upper (more ethereal) layer on distribution decreases.

Quantitative measurements of the distribution of the arsenious sulphide between the two phases have been made; they show that when one and the same colloid preparation is used, and the measurements are carried out under the same conditions as to agitation, time of standing, etc., the ratio of distribution varies continuously with the composition of the phases; and that, other things being equal, the fraction of the arsenious sulphide going into the upper layer decreases with increase in the concentration of the sulphide.

My thanks are due to Prof. W. Lash Miller, under whose direction these experiments were carried out in the University of Toronto, during the winter of 1911-1912.

NEW BOOKS

The Chemistry of the Radio-Elements, II. *By Frederick Soddy. (Monographs on Inorganic and Physical Chemistry.) 15 × 22 cm; pp. v + 46. New York: Longmans, Green & Co., 1914. Price: $0.60 net.*—This is essentially a continuation of the first monograph (16, 341); but the rapid development of the subject makes this book much the more interesting one. It is difficult to avoid quoting too much. In the introductory chapter the author says: "The chemical non-separability and identity of different radio-elements, first definitely drawn attention to in the case of radium and mesothorium I, and now shown to be the general characteristic of the radio-elements, becomes something more than the expression of experimental failures to separate and distinguish...... But now we may go on to consider the reasons underlying these facts, which make it appear that chemical non-separability and identity may be something more than merely the present limitations of the art of chemical analysis. It is necessary to reflect that, apart from radioactive evidence, the existence of more than one element in, for example, uranium or thorium could not have been suspected, to realize that chemical analysis, in general, is really not an analysis of matter into honogeneous elements at all, but rather into a number of types, homogeneous merely in their chemical behavior. Each type is recognizably different from other types by chemical methods, but may or may not be homogeneous as regards, for example, other properties, such as atomic mass and stability. The periodic law expresses a *per saltum* rather than a gradual change of chemical properties. There are a limited number only of possible chemical types represented by the separate places in the periodic table. But these types in the only cases, those of the radio-elements, where we have an entirely independent method of analysis, prove *not* to be homogeneous.

"It will be a great convenience if some new word is employed to express this newly revealed complexity of matter. The words 'isotope' and 'isotopic' suggest themselves. Henceforward a group of two or more elements occupying the same place in the periodic table, and being in consequence chemically non-separable and identical, will be referred to as a group of isotopes, and, within the group, the separate members will be referred to as isotopic. Thus ionium, thorium, and radio-thorium are isotopes, and mesothorium I isotopic with radium.

"When an α-particle is expelled it carries with it two atomic charges of positive electricity, and the expulsion of these two positive charges from the atom affects the valency of the product, as Fajans has pointed out, exactly as in ordinary electro-chemical changes of valency. If the atom were initially in Group IV, for example, its ion is tetravalent, and carries four atomic charges of positive electricity. Two such charges having been expelled with the α-particle the product is in the divalent group II non-separable from radium. The mass in this case is four units less. So with the β-ray change. The β-particle is a negative electron and the loss of this single atomic charge of negative electricity increases the positive valency of the product by one. Radium B, for example, isotopic with lead, expels a β-particle and becomes radium C, isotopic with bismuth. But the mass in this case is practically unchanged. When one α- and two β-particles are successively expelled in any order the mass is reduced by four units, but the electrical content, as defined by the relative number of positive and negative charges in the atom, is unchanged. Hence the place occupied by the atom is the same as initially, and two atoms of different mass come to have identical chemical character, that is, are isotopic. But isotopes are not confined to the members of one disintegration series. *Whenever* two or more radio-elements fall into the same place in the periodic table then, independently of all considerations as to the atomic mass, the nature of the parent element, and the sequence of changes in which they result, the elements in question are chemically non-separable and identical. As will later appear, this identity probably extends also to more of the physical properties, such as volatility and spectrum reactions.

"The place occupied by the atom in the Periodic Table is thus primarily not a function of its mass, as has hitherto been supposed, but of its electrical content, as defined, and only to a secondary extent of its mass. In consequence a chemical element is not necessarily homogeneous, and its atomic weight may be, and possibly, in general, is, a mean value rather than a natural constant. In the vertical rows, on the other hand, where the mass varies by large steps as between the various members of the same family of elements, the members are analogous but not identical in chemical properties. Thus the Periodic Law represents the chemical character of matter as the function of two variables rather than of one. Of these two variables the electrical content is the essential variable in the horizontal columns, and the mass in the vertical columns. As between the successive members of the horizontal rows, the mass, while without direct influence on the chemical properties, is indirectly of paramount importance because of its effect on the stability of the atoms. If we exclude the radio-elements and confine ourselves only to the stable or common elements, for which the Periodic Table was originally constructed, it is clear that, whether a given element is homogeneous or not, is, in the end, a question whether in that place in the Periodic Table more than one isotope is stable—that is, whether atoms of different mass can permanently exist as stable systems when in association with the particular charge necessary to give the chemical character of the particular element in question. If only one isotope is stable the element must, with lapse of time, become homogeneous, unless, as in radioactive changes, the unstable isotope is being continuously maintained. But it may not even be the general rule that only one isotope is stable. Considerations of this kind may explain the 'exceptions,' such as argon and tellurium, to the Periodic Law, and the absence of mathematical relationships between the atomic weights."

The section on the nature of the end-products in radio-active change, p. 28, contains two very interesting paragraphs.

"The question thus arises whether common lead is a homogeneous element of atomic weight 207.1, as expressed in the International List, or a mixture of the end products of the three series in various proportions. There has long been an unexplained discrepancy between the atomic weight of lead and that calculated for the end product of the radium series. For the atomic weight of radium is now known with an accuracy at least as great as that of lead, owing to the splendid work of Hönigschmid with over 1 gram of pure radium chloride. From this figure, 225.95, it is clear that the atomic weight may be taken without serious error as 226, so that the atomic weight of the end product, after the expulsion of 5 α-particles of mass four, would be 206, or 1.1 units below the value for lead. But the calculated value for both the end products of the thorium series is 232.4 minus 24, or 208.4. The end products of actinium would only be present in relatively small proportion, and may be neglected. If actinium has the same atomic weight as radium, both end products would have the atomic weight 210, which is the same as that of the end product of the minor branch of the radium series, formed in altogether negligible proportion. Hence it is clear that, *whatever be the actual case, the atomic weight of lead agrees with* what is to be expected for a mixture of the end products of the uranium and thorium series in similar proportion.....

"It is of interest to note how nearly science has approached to the solution of the problem of the alchemist. If thallium could be made to expel an α-particle, or mercury one α- and one β-particle, the product would be isotopic with gold. Though, of course, this is not yet possible, there can be little doubt that success would follow the application of sufficiently great electric potentials, of the order of some millions of volts. So far as can be seen all insulating media, even a perfect vacuum, fail at potentials far short of this, conceivably by such disintegration of the material of the electrodes."

On p. 30 we find a discussion of the origin of actinium.

"Although the long outstanding problem of the origin of actinium has not yet been cleared up, the number of possibilities to be considered is now greatly reduced, and it is to be expected that the answer to this question will soon be forthcoming. There is little doubt that actinium is a relatively short-lived radio-element, and that its period cannot be greater than a century at most. Mme. Curie, from direct observation, estimated the period provisionally as only thirty years. From the fact also that intensely active preparations of it have been prepared, it scarcely can be a primary element, and the first question to be considered is its parent. On this point the rules give an alternative. Either it must be formed from radium, or one of its isotopes in group II.A, in a β-ray change, or from 'Eka-tantalum,' group V.A, in an α-ray change. At first, before the discovery of uranium X_2, the writer suggested that the unknown product of uranium X, in group V.A, might disintegrate dually, like the C members in group V.B, giving uranium II in a β-ray, and actinium in a α-ray change. This could only have remained unknown if the period of this unknown member were very long. In this case 'Eka-tantalum' would constitute a new radio-element, obtainable from minerals in quantities sufficient for chemical examination. The discovery of uranium X_2 in this place, and its short life and absence of α-radiation, disproved this view.

"An experimental examination of a preparation of radium bromide, containing 13.2 mg of radium (element), which was ten years old, and had not been subjected to any interference during that time, disproved in turn the second alternative. No trace of actinium was found to be present in the preparation, although radio-thorium in distinct amount was obtained. The origin of this radio-thorium, presumably, is the minute amount of thorium which is known to be present in Joachimsthal pitchblende, from which the radium was extracted.

Mesothorium I, isotopic with radium, would thus be present, and would produce radio-thorium. Since radio-actinium is isotopic with radio-thorium, the absence of any indication of actinium, though radio-thorium was detected, is a guarantee that no appreciable amount of actinium can have been formed. The conclusion was reached that actinium cannot be produced from radium unless it has a period of at least 15 million years, which is practically impossible, as this would mean that there must be about 170 grams of it per ton of uranium in minerals, and that the α-activity of pure actinium in equilibrium with its products could never be greater than 1650 times that of uranium.

"It has been supposed that uranium X_1, rather than uranium X_2, might undergo the dual disintegration, in both modes, with expulsion of β-rays, producing two isotopes, therefore, in group V.A, one of which would be uranium X_2, and the other the missing parent of actinium. Once, however, the possibility of a dual change is admitted, giving the same kind of rays in both modes of disintegration, other alternatives can be framed. It seems extremely likely that some such change does occur.

"At present the most probable theory is connected with the existence of uranium Y, which Antonoff claimed to have discovered in 1911. The effect on which he based this conclusion was that the soft β-radiation of uranium X decays, in certain cases, abnormally rapidly for the first few days after separation from uranium. This effect has been called in question, but repeated and reaffirmed by Antonoff, and has recently been independently confirmed by the author so far as the main result is concerned. But if it is due to the existence of a separate product, uranium Y, this product appears now to be isotopic with uranium X_1, and to be formed directly from uranium, either I or II, presumably in a branch α-ray change. Antonoff states that the proportion of β-radiation contributed by uranium Y is of the right order to be expected if it is the first member of the actinium branch series, and this view also is independently supported. If uranium Y exists and is the parent of actinium, one α- and one β-particle must be expelled in the passage from group IV.A (uranium Y) to group III.A (actinium). So far there is, however, no evidence of the α-ray change."

On page 34 the author first outlines Sir Joseph Thomson's method for determining the masses of the positive ions in ultra-rarefied gas under the action of the electric discharge.

"Several ions were so recognized, corresponding with no previously known particle. Some of these, notably 'X_3,' which is now regarded as H_3, the hydrogen analogue of ozone, are probably new molecular species, highly interesting in themselves, but not directly connected with the present subject.

"In the case of the element neon, in addition to the known atom of mass about 20 a second was discovered of mass, about 22 which could not be ascribed to any known element. In consequence, an investigation of atmospheric neon was made by F. W. Aston, and a preliminary communication of the results was made at the 1913 British Association meeting at Birmingham. A prolonged series of fractionations by the use of cold charcoal did not affect the density of the neon, or the relative amount of the heavier constituent, as shown by the positive ray method of analysis. Then a series of fractional diffusions, coupled with density determinations, was carried out, which resulted in a partial separation of the two constituents, as attested by a change of density. The elements appear to be identical in all their properties except atomic weight, and no change in the spectrum corresponding with the change of density has been observed. The continuation of these experiments, which, naturally, are long and laborious should thus furnish valuable evidence on the questions discussed in this monograph, and particularly as to whether isotopes have the same physical properties apart from those depending directly upon molecular mass."

An interesting discussion of the argon gases is to be found on p. 43.

"The chemical inertness of the inert gases and the zero number of the family in the periodic grouping cannot therefore mean that these elements have no detachable electrons, but rather that the electrons are not detached by chemical agencies.

"A suggestion was made by Armstrong, as long ago as 1895, that the molecules of the argon gases are made up of more than one atom with such intense affinity for one another that they are destitute of external combining power, and that in consequence we do not know either their atomic weight or position in the Periodic Table. On the other hand, to-day the monatomicity of the argon gases is accepted for an immense variety of reasons, in addition to those originally available. Indeed, it is directly proved by radio-active evidence of the most varied description, both in connection with the volume occupied by the emanation and the helium produced in a known time from radium, for which the number of atoms disintegrating has been counted; by the density of the emanation, as shown by direct and indirect diffusion methods; by the fact that the stopping power of helium is in accord with Bragg's atomic square-root law, and is nearly the same as that of hydrogen, though its density is twice as great and lastly, by the periodic law generalization here dealt with, which confirms the zero position assigned to the inert gases. But Armstrong's suggestion contains the germ of an idea which serves to explain the chemical inertness of the argon gases. Instead of supposing that the atoms of the argon gases have an intense affinity for one another, it may be supposed that this intense and overwhelming affinity exists between the single argon atom and its detachable electrons. Just as chemists now explain many of the properties of nitrogen and its compounds as being due to a preference of the nitrogen atoms for one another in their combinations rather than for any other atom, so we may regard the chemical inertness of argon as conditioned by its preference for electricity rather than for matter. It will not part with its detachable electrons to chlorine, to form compounds of the type ACl_2, because its affinity for the unattached electron is greater than that for the electron attached to a chlorine atom, that is, for chlorion.

"Considerations of this character make it clear that the figures attached to the various families of the Periodic Table are relative rather than absolute. They represent not so much the absolute number of detachable electrons in the outer atomic ring as the number which one atom will succeed in detaching from another, the absolute number present in the ring being unknown."

Wilder D. Bancroft

Rays of Positive Electricity and their Application to Chemical Analysis. *By Sir J. J. Thomson. 16 X 22 cm; pp. v + 132. New York: Longmans, Green & Co., 1913. Price: $1.40 net.*—In the preface the author says: "I have described at some length the application of Positive Rays to chemical analysis; one of the main reasons for writing this book was the hope that it might induce others and especially chemists, to try this method of analysis. I feel sure that there are many problems in Chemistry which could be solved with far greater ease by this than by any other method. The method is surprisingly sensitive more so than that of Spectrum Analysis, requires an infinitesimal amount of material, and does not require this to be specially purified: the technique is not difficult if appliances for producing high vacua are available."

The book is an extraordinarily interesting one and I hope that the quotations, pp. 37, 49, 53, 65, 67, 84, 96, 99, will give some idea of the scope.

"The question arises whether the corpuscles which produce the secondaries by neutralizing a positively charged particle or ionizing a neutral one are free, or are those bound up in the molecules of the gas through which the positive rays are traveling. There are several reasons for thinking that the latter hypothesis is the more probable one.

"For if the corpuscles which neutralize the positive particles are free they should be removed by a strong electric field which ought therefore to diminish the brightness of the secondaries. I have, however, never been able to detect an effect of this kind.

"Again if free corpuscles were those which neutralized the positively charged particles, the distance such a particle would travel before it got neutralized would depend only upon the density of the free corpuscles. Now this density depends upon the amount of ionization produced by the positive rays after they have passed through the cathode; this will vary with the number of these rays as well as with the pressure and nature of the gas through which they travel. Consequently the distance a positive particle has to travel before it gets neutralized will depend upon other things besides the pressure and character of the gas, and will not therefore have a very close connection with the free path of a molecule of this gas. Wien, who has made a very complete study of the distance a charged particle travels before it gets neutralized, finds that it is of the same order of magnitude as this free path and does not depend upon the number of free corpuscles. This is in favor of the view that the corpuscles which neutralize the positive particles are not free, the process of neutralization seems to be that the positive particles move through the molecules of the gas and pluck out of them the corpuscles required for neutralization.

"Again, we conclude for similar reasons that the corpuscles which ionize a neutral particle are not free but bound up in the molecules of the gas through which the positive rays pass. These rays, like the α-particles, seem to be able to pass right through the molecules, and Königsberger and Kutschewski have shown that when moving through a gas they suffer little diminution in velocity until they are nearly at the end of their path. If the corpuscles which neutralize the positive particles are not free but are in the molecules of the gas through which these particles are passing, we can understand why there is a lower as well as upper limit to the velocity of the particles which give rise to the secondaries due to particles which have been neutralized while passing through the electric and magnetic fields. For on this view the particle before it can be neutralized has to detach a corpuscle from an atom or molecule. To do this requires the expenditure of a definite amount of work which has to be done on the corpuscle by the particle. The energy communicated to the corpuscle depends on the velocity of the particle and unless this velocity reaches a definite value the corpuscle will not get enough energy to escape from the molecule and will thus be unable to neutralize the particle.

"The question now arises as to how the mercury atom acquires these very various charges. Can an atom of mercury when ionized lose any number of corpuscles from one to eight, or does it always lose a definite number? Take for example a mercury atom with five positive charges: has it got into this condition by losing five charges when it was ionized, or did it originally lose the maximum number eight and regain three subsequently? The photographs suggest, I think, that the second supposition is the correct one, and that in the discharge tube there are two and only two kinds of ionization. By one of these kinds the mercury atom loses one corpuscle, by the other eight.

"The maximum number of charges carried by a multiply charged atom does not seem to be related to any chemical property of the atom such as its valency, but to depend mainly on the atomic weight; thus mercury, the most massive atom on which observations have been made, can have as many as eight charges, crypton atomic weight (82) four or five, argon atomic weight (40) three, neon atomic weight (20) two, nitrogen atomic weight (14), and oxygen (16), two, perhaps in rare cases three, helium also occurs with two charges; the multiple charge has been found on the atoms of all the elements tested with the very suggestive exception of hydrogen: no hydrogen atom with more than one charge has ever been observed, though as the hydrogen lines occur practically on every plate more observations have been made on the hydrogen lines than on those of any other element.

"When there are on the plates lines corresponding to atoms of the same element with one, two, or three charges, then the larger the number of charges the fainter the line. Judging from the intensity of the lines we should conclude that the number of multiply charged atoms is only a small fraction of the number with one charge. The ratio of the number of atoms which have only one charge to that of those which have two or more charges is very variable and depends on conditions which are not yet fully understood. For example, in the case of the carbon atom this ratio seems to depend to a very great extent on the type of gaseous carbon compound in the discharge tube. With some hydrocarbons the doubly charged carbon atoms are relatively much brighter than with others. Again, in the case of oxygen I have found that the purer the oxygen the fainter the line due to the doubly charged oxygen atom in comparison with that due to the atom with only one charge. It would seem that atoms torn from chemical compounds were more likely to have a double charge than those obtained from a molecule of the element. Chemical combination can not, however, be the only means by which the atoms acquire multiple charges, for the atoms of the inert monatomic gases, neon, argon and crypton, are remarkable for the ease with which they acquire multiple charges.

"I have not been able to find any case in which a molecule of either an elementary or compound gas carries a double charge. The line corresponding to the molecule of nitrogen appears on some plates to have a prolongation towards the vertical axis; this would imply a double charge on the nitrogen molecule. I am inclined to think that this prolongation is not really due to the nitrogen molecule, but to the atom of aluminium, as m/e for this atom is 27.5, and for the nitrogen molecule 28, the lines would be so close together that it would be difficult to differentiate them....

"Chemical action, unless accompanied by high temperature, has not been shown to give conductivity. The very vigorous combination of hydrogen and chlorine under sunlight seems to have absolutely no effect on the conductivity of the mixture, and this is a strong reason for supposing that the atoms in the molecule are not charged.

"It is true that chemical actions vigorous enough to raise the gases to a very high temperature, such as, for example, the combination of hydrogen and oxygen in the oxy-hydrogen flame, the oxidation in a Bunsen flame, the burning of CO and so on, make the reacting gases good conductors of electricity. This conductivity seems, however, from the result of recent experiments, to be due to the high temperatures produced by the chemical action rather than to the action itself. The conductivity cannot be due to the molecule being dissociated into positively and negatively electrified atoms, for the determinations of the mobility of the negatively electrified particles in flames and gases at a very high temperature show that it is much larger than would be possible if these particles had masses comparable with that of even the lightest atom. These negatively electrified particles are corpuscles, not atoms, and the electrical conductivity of gases at high temperatures is due to the dissociation of the molecules and atoms into positively charged molecules and atoms and negatively-electrified corpuscles, and not to a dissociation such as occurs in solution when the electrified bodies are positively and negatively electrified atoms. The conductivity of hot gases seems to be an example of the emission of corpuscles from hot bodies, rather than to be directly connected with chemical combination. We know that when we raise solids such as metals, or still better, certain oxides to a high temperature they give out copious streams of corpuscles, and the conductivity of flames is better explained by supposing that gases possess this property to some extent than by attributing it to chemical action alone.

"We are led by these results to regard the electrical forces which keep the atoms in a molecule together as due not to one atom being charged positively and the other negatively, but to the displacement of the positive and negative electricity in each atom. Thus each atom acts like an electrical doublet and abstracts another atom in much the same way that two magnets attract each other......

"We see that in some gases we have both atoms and molecules, in others only atoms. We can infer from the study of the curves produced by the positive rays that helium, for example, is a monatomic gas, hydrogen and oxygen di-atomic.

"The rays show too that the atoms and molecules of the gases can be charged with electricity; all of them, as far as we know, with positive electricity, some of the atoms with negative as well. The circumstances are very unfavorable for particles in the positive rays to get a negative charge, and we must not conclude that because an atom or molecule has not been observed to acquire a negative charge when in the positive rays it is incapable of doing so under more favorable circumstances.

"We have seen too that the atoms of all the elements except hydrogen can acquire more than one unit of positive charge. The maximum number of such units seems to depend on the atomic weight of the atom, for mercury, the heaviest *atom yet investigated, it is as large as eight, for* krypton four or five, for oxygen two, and so on. No undoubted case of a double charge on a molecule, whether of an element or a compound, has yet been observed. In addition to the atoms and molecules of recognized elements these rays reveal the existence of radicles and other combinations which are not known to exist permanently in the free state. Thus the positive rays from marsh gas CH_4 show, in addition to the atom amd molecule of hydrogen and the atom of carbon, the systems CH_1, CH_2, CH_3, CH_4. The radicle OH with a negative charge has also been found when water vapor was in the tube. We can detect by this method systems which have a very transitory existence, for they need only last long enough to travel from the discharge tube to the photographic plate, a journey which takes less than the millionth of a second.

"Again the rays show that with those compounds of carbon, which contain two or more carbon atoms united by bonds, two carbon atoms connected together are found in the positive rays, and since they are found with a negative as well as with a positive charge the two carbon atoms united in this way cannot be saturated......

"The positively charged particles, which we have hitherto considered, originate in the neighborhood of the cathode. Gehrcke and Reichenheim have discovered rays of positively charged particles which start from the anode. Their attention was called to these rays by noticing that a pencil of yellow light streamed from a point on the anode of a tube with which they were working. It was found that there had been a speck of sodium chloride at the points on the anode from which the pencil started. They got these rays developed to a much greater extent when they used for the anode a piece of platinum foil with a little pocket in which various salts could be placed. The foil was in circuit with a battery insulated from the one used to send the current through the discharge tube; this battery was for the purpose of raising the anode to a red heat, as these rays are not developed unless this electrode is at a high temperature. The current through the tube was produced by a battery giving a potential difference of about 300 volts which, as a Wehnelt cathode was used, was sufficient to send a very considerable current through the tube; the pressure in the tube was very low. The rays were well developed in this tube when NaCl, LiCl, KCl and the chlorides of Cu, Sr, Ba, In, were placed in the pocket. The color of the rays corresponded with the color given to flames by the salt. They did not get any effect when the oxides of calcium or barium were put in the pocket; these oxides are known when hot to give out large streams of negatively electrified corpuscles and for this reason are used for Wehnelt cathodes. These rays are apparently only given out by the salts of the metals and not by the metals themselves; they are called Anode rays.....

"Stark's experiments have shown that the source of the series lines is one of the constituents of the positive rays: the question is, which constituent. We have seen that in hydrogen, for example, we have positively and negatively charged atoms, as well as neutral ones: we have also positively charged and neutral molecules. There is considerable difference of opinion as to which of these is responsible for the series lines in the hydrogen spectrum. All theories concur in regarding the atom and not the molecule as the source of these lines, but according to Wien's theory the atom radiates when in the neutral state, while Stark maintains that the radiation is emitted when the atom has a positive charge: according to his view the lines emitted by the neutral atom are far away in the ultra-violet.....

"The spectroscopy of the positive rays suggest some very interesting questions, as, for example, what kind of light do the molecules emit? In the positive rays in hydrogen the molecules frequently outnumber the atoms, but no radiation that can be attributed to the molecules has yet been detected. The second spectrum of hydrogen is there, but as it does not show the Döppler effect it cannot be due to the molecules. It would seem as if the molecules must either give rise to a continuous spectrum or else to one in the infra-red.

"As the second spectrum of hydrogen is present when the positive rays pass through a gas, but does not show any displacement, it must arise from some process in which the moving particles do not take part, such for example as a combination of a positive atom with a negative one (not with a corpuscle) to form a neutral molecule.

"Stark has detected by the increased Döppler effect lines due to the doubly and triply charged atoms of mercury and to the doubly charged atom of helium. He finds that the lines given out by the multiply charged atoms belong to different series in Paschen and Runge's classification from those given out by atoms with only one charge."

Wilder D. Bancroft

Handbuch der Mineralchemie. *By C. Doelter. Vol. II, Part V. 18 × 25 cm; pp. 248. Dresden: Theodor Steinkopff, 1914. Price, $9.10 marks.*—This number completes the second volume and contains the title-page together with name index and subject index. Nephrite and jadeite are included in this number, thus finishing the discussion of the amphiboles. There is a chapter on manganese and ferrous orthosilicates, followed by one on the orthosilicates of beryllium, manganese, and iron which contain sulphur, in other words helvin and danalith. Thirty pages are devoted to the metasilicates of manganese and iron after which come shorter sections on the silicates of nickel, copper, zinc, and lead.

Wilder D. Bancroft

Metallographie. *By Cecil H. Desch. Translated by F. Caspari. (Handbuch der angewandten physikalischen Chemie. Band XII.) 17 × 25 cm; pp. v + 265. Leipzig: Johann Ambrosius Barth, 1914. Price: paper, 14 marks; bound, 15 marks.*—This is a translation of the English edition (14, 792) with some changes to take account of the recent work. There are many more literature references in the German edition. In the case of the iron-carbon diagram, the author has taken a distinct step backward. He now gives four lines to Upton's work where he gave four pages before. The section on the theory of polishing, p. 209, has been amplified though not much changed. Beilby's theory of the amorphous states is accepted as true and there is a complete disregard of the experiments on electrolytic deposition of metals. In spite of these defects the book is a valuable one and a welcome addition to the series. *Wilder D. Bancroft*

THE ELECTROLYTIC DETERMINATION OF NICKEL

BY W. JUDSON MARSH

Among the methods proposed for the electrolytic determination of nickel, that of A. Classen, who uses a solution containing an excess of ammonium oxalate, is quite generally recommended by the standard text books on quantitative analysis. The method is also mentioned favorably in some of the books on electro-analysis. Work in this laboratory had already shown that this method was not especially accurate or easy to carry out and so it was decided to repeat certain work already carried out and to test out certain other suggestions made by Professor Bancroft, of this laboratory.

Much work has already been done on the electrolytic determination of nickel and its congener cobalt, but a complete bibliography of such research is not required in the present article.[1]

In 1902 Akerberg[2] made a study of the rapidity of the electrolytic decomposition of oxalic acid in the presence of sulphuric acid, in which he came to the following conclusions:

1. In H_2SO_4 solution oxalic acid is but little decomposed by the electric current.
2. Platinized platinum anodes cause the decomposition of oxalic acid, i. e., it is oxidized at the anode.
3. Reaction is monomolecular, i. e.,

$$H_2C_2O_4 + O \longrightarrow H_2O = 2CO_2$$

In 1909 G. Lambris[3] reported a further research on "The Taking-up of Carbon by Metals in the Case of Electrolysis from Aqueous Solution, with especial Reference to Nickel." In this article the author reviews previous work on the electrolytic deposition of carbon and describes his own experiments minutely. It had been found that certain carbona-

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[1] Zeit. anal. Chem., 19, 314 (1880).

[2] Zeit. anorg. Chem., 31, 161 (1902).

[3] Zeit. Elektrochemie, 15, 973 (1909).

ceous material was deposited along with nickel in the method suggested by Classen and the author attacked the problem of explaining and preventing this. He came to the following conclusions:

1. The absorption of carbon by the nickel is entirely due to a gas reaction.

2. The gases which introduce the carbon are CO, CO_2 and C_2H_2. Such gases as are reduced beyond C_2H_2 do not introduce any carbon.

3. Oxalic acid is partly reduced to C_2H_2 upon platinum and nickel, but not when Cu, Fe, or Sn cathodes are used. Therefore C_2H_2 is only a carrier of carbon to metals (cathodes) in electrolysis.

4. The carbon in electrolytic Ni is present in the form of carbide.

5. A porous porcelain cup placed about the cathode prevents the deposition of carbon with the nickel.

6. The introduction of $(NH_4)_2CO_3$, C_2H_2, CO_2 and CO into the cathode compartment causes the separation of carbon along with nickel.

7. When C_2H_2 is used, the carbon content is very nearly the same as in case of the oxalate electrolysis.

Lambris also did much other work on the nature of this carbonaceous matter deposited, and came to the conclusion that it existed as a carbide, which, when separated out for analysis, invariably yielded heavy hydrocarbons, light hydrocarbons, carbon dioxide, and hydrogen on treatment with dilute HCl. He also concluded that certain small amounts of ammonium salts were held (adsorbed) by the carbon itself, which separates on dissolving the metal deposit. He was able to obtain results from 2 to 2.5 percent in excess of the weight of nickel known to be present (e. g., 8.6 mg carbon in a deposit of 0.4403 gram nickel).

Classen's method is described in his book, "Quantitative Analysis by Electrolysis" (1903 edit., p. 160) "Metal present as sulphate.

Substance added: 6 to 8 grams ammonium oxalate.

Total volume of solution: 120 cc.
Temperature: 60° to 70°.
Current density at cathode: N. D. = 1.0 ampere.
Potential difference: 3 to 4 volts.
Time required: about 3 hours."

Classen advises the use of ammonium sulphide to test the solution for the last traces of nickel. His book gives short descriptions of the methods of Fresenius and Bergmann $\{(NH_4)_2SO_4$ + free NH_4OH in solution$\}$, Oettel (chloride solutions), Smith (cyanide solution). Fernberger and Smith (phosphate solution), Campbell and Andrews (phosphate and excess NH_4OH solution) and Gooch and Medway $\{(NH_4)_2SO_4 + NH_4OH$ with rapid rotation$\}$. He gives no further data as to the conditions or results of his method for nickel; but under his oxalate method for tin, which is quite similar, he claims that the method is sufficiently accurate to yield results suitable for the atomic weight determination of tin (page 212).

Attempts have been made in this laboratory to use this oxalate method for the determination of nickel, cobalt, and tin, but only in the last-mentioned case (tin) has it proved at all suitable for accurate electroanalysis. Briefly, some of the disadvantages or inconveniences of the method are: the use of special and expensive apparatus, the necessity of plating the platinum dish cathode with copper on silver, the long and uncertain time required for a determination (3 to 7 hours); extra trouble of heating the solution to a constant temperature, evaporation of the electrolyte and the consequent tendency of salts to "crawl" out on the stem of the anode and upper edges of the dish, the separation of the nickel as peroxide on the anode toward the end of the run, the necessity of siphoning out the solution and adding distilled water at the end of the run and the uncertainty as to results obtained, these usually running high due to the codeposition of carbonaceous material.

In the description of the method no mention is made of this last and most troublesome tendency, and, of course, no suggestion as to any means of obviating it. With this in mind the present research was begun with the following objects in view:

1. Repetition of certain parts of the work of Akerberg and Lambris.
2. To find the conditions which give the worst results, i. e., the highest percent of deposited carbon, etc.
3. To find the conditions which give the best results by this method.
4. If possible to modify the method so as to render it more accurate and rapid.
5. To test out the effect of certain addition substances.
6. If not possible to improve the method sufficiently, to work out and give in detail some simpler, more rapid, and more accurate method.

Very little need be said as to the repetitions of work by Akerberg. From the statement of the former to the effect that oxalic acid was but little decomposed by the current when sulphuric acid was present, it was thought that possibly the presence of the sulphate ion might prevent the break-up and consequent oxidation of the oxalate ion and consequently do away with the deposition of carbon at the cathode, the theory being that the oxalic acid is oxidized at the anode to $2CO_2$ and H_2O, and that the CO_2 then diffuses, in part, to the cathode where it is reduced and some acetylene is formed which then may react with the freshly deposited nickel to form a carbide of nickel. The use of H_2SO_4 in this case is not permissible and so $(NH_4)_2SO_4$ was tried, without the desired result. A solution, the Ni content of which had been previously determined by the excellent dimethylglyoxime method of Brunck,[1] was found to contain 0.1698 gram Ni per 50 cc solution. Using the apparatus and conditions recommended by Classen with additions of 3, 5, and 10 grams $(NH_4)_2SO_4$, deposits were obtained weighing 0.1730 gram, 0.1748 gram, 0.1719 gram. In every case 50 cc samples

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[1] Zeit. angew. Chemie, 20II, 1844 (1907).

were taken carefully from a reservoir-burette bottle (at or very near 20° C).

An attempt was next made to repeat the work in which Lambris obtained the highest amounts of carbon along with the nickel deposit—the amount being judged by the difference in weight of the deposit and the weight of nickel in the solution used (i. e., 0.1698 gram Ni per 50 cc solution). Unsuccessful attempts were made to cause the nickel of the deposit to dissolve in $KCl.CuCl_2.2H_2O$ solution as used in the determination of total carbon in iron or steel. It was found that hydrochloric acid of a concentration sufficient to dissolve the deposit left little or no solid residue of carbonaceous material, which is in accord with the findings of Lambris. It was found possible, however, to obtain some of this carbonaceous material by adding distilled water and then nitric acid drop-wise until the deposit began to dissolve very slowly as shown by the evolution of small gas bubbles from the surface of the deposit. The reaction, however, tended to speed up as heat was evolved and more distilled water was added. With care it was found possible to obtain from $^1/_2$ to $^2/_3$ of the weight in excess of the true weight of nickel. The amount of this solid residue, however, was necessarily small (a few milligrams) and, when analyzed by the oxygen combustion method, the results were not very satisfactory, indicating that the product was from 77.5 percent to 91.2 percent carbon. This was not considered surprising, however, as the material seemed to vary considerably in color, size of particles, and physical form. Usually it was nearly black, but on two occasions it appeared distinctly brownish. Usually it was finely divided and granular in appearance, but sometimes it was flocculent and filmy. It seemed to cling tenaciously to small amounts of ammonium salts. Lambris reported that he was unable to notice any carbon when Cu, Fe, or Sn cathodes were used. In this laboratory very considerable amounts of carbon have been found when a solution of copper carbonate is dissolved in a slight excess of acetic acid and the solution electrolyzed, using a potential difference of 2.5 to 3 volts and a current density of N. D_{100} = 1 to 2 amperes in a total volume of 150 cc. Also in Classen's oxalate method for tin, numerous high results have been obtained. A tin solution made from Kahlbaum's C. P. tin so that 50 cc were exactly equal to 0.3000 gram Sn gave the following results:

Series I	Series II
0.3008	0.3036
0.3010	0.3040
0.3007	0.3041

The results in the second series were higher than those in Series I, because they were run from 15 minutes to one-half hour longer than those in Series I. Conditions used were 4 grams $(NH_4)_2C_2O_4$, 8 grams $H_2C_2O_4$ at 1 ampere per 100 sq. cm and 3 volts, using a rotating copper gauze cathode (see below). In spite of Classen's note to the contrary, this method does not seem well suited to the determination of the atomic weight of tin. If the electrolysis was allowed to run for one hour, the results were fairly good, but they seemed to go much too high when allowed to run longer.

In the introductory part of his book Classen recognized several phenomena of a nature apparently similar to the above cases in which the oxalate radical seems to furnish a source of the carbon deposited with metals. For example (on page 39 of his book), he noted that carbon dioxide was formed by the oxidation of the acetic acid radical, which then might also yield ethane and even ethylene. Octane, isobutylene, ethylene, carbon monoxide, formaldehyde, formic acid, etc., he said were also formed on the break-up of various organic acids.

The attempt to find conditions which yield the highest amounts of deposited carbon gave no new results. The percentages of carbon deposited, as indicated by excess weight of the deposit, were of much the same magnitude as those obtained by Lambris, i. e., about 2.5 percent.

Next, numerous runs were made in an endeavor to improve the method, but without much success. When the temperature is kept close to 50° and water is added from time to time to replace that lost by evaporation, the method gives fair results if allowed to run 2.5 to 3 hours. These results are usually a little low, however, as some nickel remains in the solution. This amount is too small to be shown by the $(NH_4)_2S$ test, but shows up readily on using dimethylglyoxime as a spot-test reagent. This indicator is now used in this laboratory as an end test for both nickel and cobalt, giving a reddish pink coloration with CO and a pink precipitate with Ni (in presence of NH_4OH or NaAc). Variation of the amount of $(NH_4)_2C_2O_4$ had but little effect as long as the amount present exceeded 5 grams per 120 cc of solution containing ca. 0.17 gram Ni. The addition of 1–2 gram of urea had a beneficial effect. The tendency for NiO_2 to separate at the anode toward the end of the run was eliminated by addition of a little NH_4OH or "glycerol mixture" (E. F. Smith: Electro-Analysis) or by decreasing the current and voltage for a few minutes near the end of the run.

Since none of the above changes improved the method sufficiently to render it as rapid and accurate as a good electrolytic method should be, it was decided to try the effect of certain addition substances (known to electroplaters as "dopes"). It was thought that some reducing agent might be found which would react with the oxygen formed at the anode and by so doing decrease the time required and the amount of carbon dioxide formed and consequently the amount of carbon deposited. Those tried were hydrazine sulphate, hydroxylamine sulphate, sodium nitrite and sodium sulphite. Of the first three hydrazine sulphate was the only one to produce a noticeable effect. When it was added to the extent of 5 grams it produced a blackening of the deposit, possibly due to the formation of nickel sulphide.

This last seems more probable in the light of the unexpected behavior of the last reducing agent, sodium sulphite. Although this has not been sufficiently investigated, it is certain that its effect is surprising and for this reason it is to be studied more thoroughly. Briefly the phenomena noticed were as follows: on addition of 5 grams of Na_2SO_3 (Baker's C. P.) and all other conditions being those employed by Classen, a black flocculent precipitate begins to form almost as soon as the circuit is closed. This precipitate increases rapidly in amount and the odor of hydrogen sulphide is perceived. Thinking that this phenomenon might be due to some chemical reaction, a blank was made which showed this not to be true. Other blanks were run, the first showing no such behavior when the 6 to 8 grams $(NH_4)_2C_2O_4$ was electrolyzed with 5 grams Na_2SO_3 in 120 cc of water at 50° C, and the second also gave a negative result when the nickel solution and 5 grams Na_2SO_3 were electrolyzed, all other conditions being the same (except that no $(NH_4)_2C_2O_4$ was present).

At first it was thought that this precipitate might be some carbonaceous material such as that which deposited with the nickel, but on filtering it off and washing it, the material dissolved quite easily in warm 6*N* HCl with evolution of H_2S and the formation of the characteristic green solution of nickel chloride. It was evident that 120 cc of a nickel sulphate solution is quickly reduced to black NiS in the presence of 6 to 8 grams $(NH_4)_2C_2O_4$ and 5 grams Na_2SO_3.

Then, on washing out the Classen dish in which this run had been started, it was noticed that a firm deposit had been formed on the copper with which the dish had been previously plated. This deposit appeared much like the ordinary good nickel deposit, but was somewhat darker in color. Previously certain very thin films of iridescent metallic sheen had been noted floating off from the dish cathode when the solution was rapidly stirred. These films were very similar to those often noticed when H_2S is passed into solutions for the precipitation of metals in qualitative analysis, especially in case of lead solutions. Although this work has not yet been confirmed, it seems reasonably certain that these films as well as the firm, even, metallic deposit on the copper were both nickel sulphide. It may be possible that in dissolving the deposit with 1 : 1 HNO_3 some error of manipulation was made, but it is certain that after washing the deposit carefully, a considerable amount of hydrogen sulphide was given off when the nitric acid was diluted. This might seem to indicate that a form of nickel sulphide not unlike the mineral Millerite (sulphide of Ni) had been formed. This mineral (according to Dana's Mineralogy, pp. 70–71) is said to have a "grayish iridescent tarnish" and it is claimed to have been prepared artificially.[1]

The addition of small amounts of urea (1 to 2 grams) seemed to cut down the time required for the completion of a determination, but no effect on the carbon deposition was noted.

Finally it seemed possible that a decrease in the size of the anode might tend to lessen the oxidizing effect at that electrode, as the oxygen would be less liable to remain in the solution. When, however, a platinum wire was used as anode, it was found that the consequent increase in anode density augmented the tendency of nickel to deposit as peroxide on the anode. For this reason it was necessary to abandon this idea.

At this point it was thought best to test out some other method along with a simpler form of apparatus. It was hoped to adopt and modify some of the successful methods of the electroplating industry so as to work out a procedure satisfactory to the analyst. Thinking that such a method would be more liable to yield the desired results if the solution should be as nearly neutral and of as unchanging composition as possible, a number of plating methods were tried out including a boric acid solution, the same with various addition substances, a solution containing an excess of borax, a solution containing an excess of sodium pyro-phosphate and ammonia, a solution containing a slight amount of formic acid and an excess of sodium formate, a solution containing a small amount of free lactic acid and an excess of lactate (NH_4 lactate), a solution containing free phosphoric acid and

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[1] Weinschenk: Zeit. Kryst., 17, 500 (1890); Baubigny: Syn. Min., 4, 168 (1881).

NaH_2PO_4, and finally the well known ammonium sulphate-ammonia solution.[1]

Of all the solutions above mentioned, the last was the most satisfactory. Some would not run to completion, some gave good deposits at first but unsuitable for analytical purposes due to "burning," etc., at the end, most of them were very slow, etc. After considerable work on this method the following very satisfactory solution was found:

Nickel present (about 0.2000 gram) as $(NH_4)_2SO_4.NiSO_4.6H_2O$.

Ammonium hydroxide 15-20 cc (Sp. Gr. 0.96).

Ammonium sulphate 5 grams.

Amperage 0.8 ± 0.1.

Potential difference 3.5 ± 0.2 volts.

Time required about 25 minutes. Room temperature.

Nitric acid, nitrates, and chlorides must not be present. Total volume of solution made up with H_2O to 200 cc.

Electrolyze in a 350 cc beaker using a 10 gram platinum-wire gauze flag anode (52 mesh and 6 × 4.5 cm) and a rotating (550-650 R. P. M.) pure Cu gauze (50 mesh and 5 cm high × 3 cm diameter) cathode. This electrode combination is much less expensive than the Classen dish and disk of platinum, requiring only one-fifth as much platinum as the latter. The Cu wire gauze cathode can be made easily, quickly, and cheaply. Stiff, twisted Cu wire is used for the stems and small Cu tacks are used to rivet the gauze together. One such cathode can be used for a great many determinations, as a fresh surface for deposition may be obtained by dipping a used cathode in 1 : 1 HNO_3 for a few moments. When well made and properly handled the cathodes which cost but a few cents and a few minutes work give results exactly as good as any platinum cathode. This makes it possible to run many more determinations than is usually possible with more expensive forms of apparatus. These cathodes have also been used successfully in the laboratory for the determination of copper, tin, cobalt, cadmium, bis-

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[1] E. F. Smith: Electro-Analysis, 122-130.

muth, silver, and zinc. They have also been used in combination with the platinum wire gauze anodes for the determination of lead and manganese, both of which are deposited on the anode as peroxides.

The accompanying table of results obtained by eleven different students using this method will give some idea as to the value of the method to those not especially skilled in quantitative manipulations.

ELECTROLYTIC DETERMINATION OF NICKEL

Solution = $NiSO_4(NH_4)_2SO_4.6H_2O$ (ca. 21 g. per liter)
Weight of nickel in each run[1] = 0.1336 g. + 15 cc NH_4OH, sp. g. 0.96; diluted to 200 cc
50 cc nickel solution. Potential difference 3.5 ± 0.2 volts

Current Ampere	Time Minutes	Weight of Ni found Gram	Error of method Gram
0.7	20	0.1359	+0.0023
0.7	20	0.1337	+0.0001
0.7	20	0.1296	—0.0040
0.7	20	0.1340	+0.0004
0.7	20	0.1310	—0.0026
0.8	30	0.1348	+0.0012
0.8	30	0.1338	+0.0002
0.8	30	0.1346	+0.0010
0.8	25	0.1334	—0.0002
0.8	25	0.1334	—0.0002
0.8	25	0.1332	—0.0004
0.8	25	0.1338	+0.0002
0.7	25	0.1341	+0.0005
0.7	25	0.1336	0.0000
0.7	25	0.1340	+0.0004
0.7	25	0.1336	0.0000
0.7	25	0.1332	—0.0004
0.7	25	0.1344	+0.0008
0.8	25	0.1339	+0.0003
0.8	25	0.1339	+0.0003
0.8	30	0.1344	+0.0008
0.8	30	0.1331	—0.0005
Av. 0.75	25	0.1336	+0.0002

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[1] The amount of nickel per 50 cc of solution (0.1336) was determined by averaging a series of fine determinations of Ni by the dimethylglyoxime method.

The writer wishes to acknowledge and express his gratitude for the many timely suggestions of Professor Bancroft. Much valuable assistance was also rendered by Dr. G. E. F. Lundell and Mr. A. M. Hart.

Cornell University
June, 1912

A THERMOSTAT FOR LOW TEMPERATURES

BY JAMES H. WALTON, JR., AND ROY C. JUDD

In order to carry out a series of experiments on the velocity of crystallization of water, it was necessary to construct a thermostat that could be held constant at temperatures from 0° to about —20°. The apparatus that was finally devised for this purpose is described below and a cross section shown in Fig. 1.

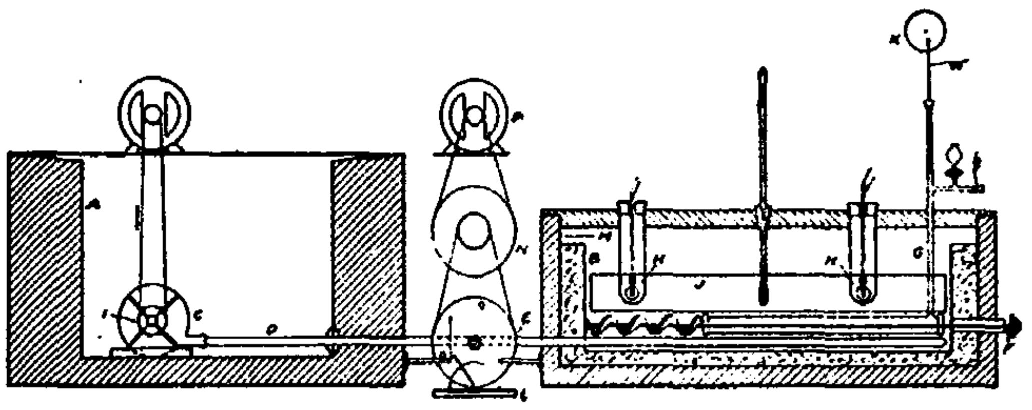

Fig. 1

The general plan consists of a primary bath A and a secondary bath B. The primary bath is filled with a mixture of ice, salt and water, which is pumped through a coil in the secondary bath. When the temperature of the solution in B becomes too low, a regulator closes a cock by means of the wheel E and shuts off the flow of the cold brine. Similarly, when B becomes too warm, the cock is opened and the flow of brine lowers the temperature.

The essential details of the apparatus are as follows: The primary bath A is eighteen inches square and fourteen inches deep. It is constructed of heavy galvanized iron and is placed in a box and insulated with a 4 inch layer of sawdust. The dimensions of the secondary bath are 25″ × 5$^1/_2$″ and 6$^1/_2$″ in depth. It is also constructed of galvanized iron and is placed in a wooden box, M. Between the bath and M is a one inch layer of felt. M is provided with a tightly fitting cover and is covered on the outside with a layer of felt about half an inch thick.

The brine from the primary bath is pumped by means of the turbine C, through D, back into A again through a return pipe that is not shown in the figure. The brine coming in at the intake of the pump passes through fine copper gauze which removes bits of straw, etc., that would clog the pump. The axle of the pump extends through a packing box to the outside of the bath. It is driven by means of the wheel I, which is connected with a one-tenth H. P. motor.

The secondary bath is agitated by a screw-shaped stirrer, F, which is driven from the outside of the bath. For a long narrow bath of this kind, this has proven the most efficient type of stirrer. A double window, J, makes it possible to observe the growth of the crystals in the tubes that are immersed in the bath. The panes of glass in this double window are about three-fourths of an inch apart. This double window has the advantage that it furnishes an air space which is an insulator and eliminates, to a considerable extent, the heating of the bath. Moreover, water vapor does not condense to ice on the outside of the glass and thus interfere with the view of the inside of the bath as is the case when a single window is used. The inside of the bath is illuminated by two 4 c. p. 6 volt incandescent bulbs, H, H, similar to those used for automobile side lamps. Considerable difficulty was experienced in finding a suitable regulator. The ordinary form of glass regulator filled with toluene is not satisfactory. The liquid in the regulator conducts the heat so slowly that there is a great lag in its operation with a consequent diminishing of the constancy of the bath. This was in part avoided by using a regulator, G, consisting of a steel tube filled with mercury. To further reduce the lag, the mechanism shown in the figure was used.[1] This consists of a slowly rotating wheel, K, to which a platinum wire is attached to an excentric

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[1] Gouy: Jour. Phys., 6, 479 (1897); see also Barnes: Phil. Trans., 199, 149 (1902).

so that it moves up and down in the stem of the regulator. When the mercury expands it makes contact with the platinum wire, an electrical connection is made that rotates the wheel E, thus opening the cock in a manner to be described shortly. This sends cold brine through the pipe D. The platinum wire, however, is slowly withdrawn from the mercury and the contact broken before the mercury is through expanding, thus compensating for the lag in the regulator. If the bath has been cooled to the desired temperature by the opening of the cock, the mercury will usually have commenced to contract by the time the platinum wire begins to descend again. This device must be regulated to suit the individual bath, the length of throw of the wire and the speed with which it moves being the factors that must be controlled.

The success of the thermostat depends upon the method of automatically opening and closing the cock that admits the cold brine. The details of the arrangement are shown in Fig. 2. The pipe D is provided with a cock, Q, which is an ordinary water cock used on faucets. To the end of the rod Y, operating this cock, a wooden wheel, E, about six inches in diameter, is secured by a nut, Z. Two rubber stoppers, S, S, are secured to E. When the wheel is turned these stop-

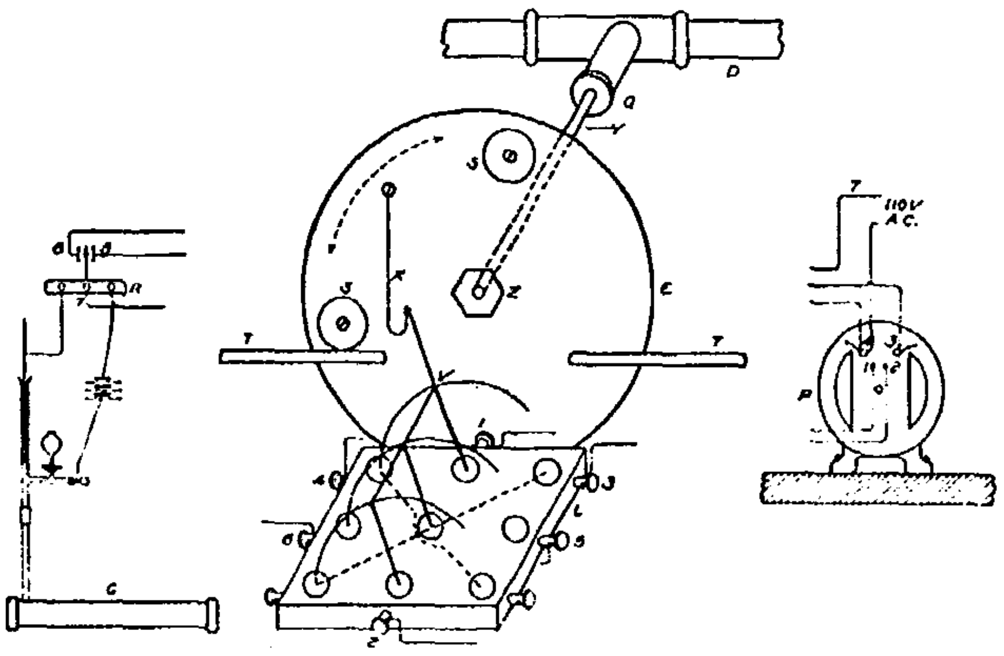

Fig. 2

pers come in contact with the "bumpers" T, T and so make it impossible for E to make a complete revolution. A nine point rocking switch, L, is connected to E by means of a string X. To bring the bath to the right temperature the nut Z, fastening E to the cock, is loosened and the cock opened enough to allow the bath to come to a temperature a few tenths of a degree above that desired. E is then turned as far as possible to the right and the nut tightened. Turning the wheel to the left will now open the cock and permit a larger stream of the cold brine to flow through the secondary bath. When the temperature of the bath becomes too high the regulator, by means of the relay R, throws the motor P, into a 110 v. A. C. circuit. This starts the motor (shown in Figs. 1 and 2) and rotates E to the left, opening the cock. The rotation of E pulls the rocker of the switch to the left and breaks the 110 v. circuit. The connections through the switch are made in such a way that as soon as the points of the rocker leave the mercury cups on the right the 110 volt circuit is broken. As soon as contact is made with the mercury cups on the left of the switch the fields of the motor are reversed.[1] The cold brine now runs through the secondary bath until the mercury in the regulator begins to contract. The current through the relay is then broken. This starts the motor P, once more, but the direction in which it turns has been reversed consequently E is rotated to the right, the cock is closed once more and the 110 volt current again shut off. For as soon as the points of the rocker leave the mercury cups at the left the 110 volt current is broken, and the fields of the motor are reversed when contact is made with the cups at the right. The making and breaking of the current by means of the regulator thus intermittently opens and closes the cock. The motor that does this is in motion only while the cock is being opened or closed and at no other time.

The binding posts or wires in Fig. 2 that are numbered

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[1] The motor used for opening and closing the cock was made by the General Electric Co. It is described as follows: Induction motor. 60 cycles. 110 volt. Type Dss. $^1/_{16}$ H. P. Speed 1800. Cat. 66931.

the same are connected directly. Thus 6 on the relay has a direct connection with 6 on the rocker switch.

The solution used in the secondary bath was made by mixing two parts of water with one part of glycerine and one part of ethyl alcohol.

In a test carried out to ascertain the constancy of this thermostat it was found that at a temperature of —12° during a run of six hours the temperature varied ±0.03°. By using a mixture of calcium chloride and ice in the primary bath it is possible to keep the secondary bath at a temperature of —25° to —30°.

The automatic cock described above may be used at temperatures above zero. For example, ice water could be substituted for the brine solution, and at higher temperatures the primary bath could be entirely replaced by a boiler generating superheated steam.

Department of Chemistry
University of Wisconsin

THE VELOCITY OF THE CRYSTALLIZATION OF UNDERCOOLED WATER

BY JAMES H. WALTON, JR., AND ROY C. JUDD

Although the velocity of crystallization of many undercooled liquids has been measured, comparatively little work has been done on the speed with which undercooled water changes to the solid phase.

Turmlirz[1] measured the velocity with which this substance crystallizes, using thin-walled tubes of 18 mm internal diameter. These tubes were filled with water and placed in a bath which was then cooled by exposure in a cold room. When a crystal of ice was brought in contact with the undercooled liquid, crystallization took place. The velocity could easily be determined by measuring the time necessary for the advancing surface of the solid phase to travel a given distance. Turmlirz's results are given in Table I, in which *t* is the number of degrees of undercooling, and V is the velocity of linear crystallization expressed in mm per second

Table I

t	V	*t*	V
—0.74	0.37	—2.71	5.77
—1.12	1.44	—2.90	7.06
—1.40	2.20	—3.20	7.47
—1.54	2.76	—3.49	10.23
—1.62	2.92	—3.64	11.28
—2.00	3.32	—4.14	16.93
—2.40	4.49	—4.20	18.15
—2.54	5.24	—4.60	22.07
—2.67	5.58	—	—

Because of spontaneous crystallization, Turmlirz was unable to make measurements below —4.6°. In the light of the interesting and important work of Tammann,[2] Marc,[3]

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[1] Sitzungsber. Wiener Akad., **103** II*a*, 226 (1894).

[2] Kristallisieren und Schmelzen, p. 131 (1903).

[3] Zeit. phys. Chem., **61**, 385 (1908); **67**, 470; **68**, 104 (1909); **73**, 685 (1910); **75**, 710 (1911).

Freundlich,[1] and others, on this subject it seemed desirable to determine the speed of crystallization of water with special reference to factors affecting it, particularly the influence of dissolved substances.

Experimental

The usual method for measuring the speed of crystallization is to undercool the substance in a tube, and at a definite temperature to cause crystallization by introducing a fragment of the solid phase. The time necessary for the crystals to fill a certain length of the tube gives the linear velocity of crystallization. To undercool water more than two or three degrees, special precautions must be taken. The water must be pure, free from dust and air, and covered with a layer of oil. Paraffine oil may be used for this purpose, although Turmlirz used turpentine in his experiments. The volume of water used should be as small as possible. Tammann[2] has shown that spontaneous crystallization is accompanied by the formation of crystalline nuclei throughout the solution. The greater the volume of liquid used the greater is the chance of these nuclei being formed. The experiments of the authors show that with the same volume of water, undercooling is more easily carried out in a flask than in a tube; the water can be cooled to a lower temperature, and there seems to be less danger of spontaneous crystallization.

In determining the velocity of crystallization of undercooled water, the following method was used: A soft-glass tube, similar to that shown in Fig. 1, was filled to the level A with freshly boiled conductivity water. Paraffine oil that had been carefully washed was then placed in each arm of the

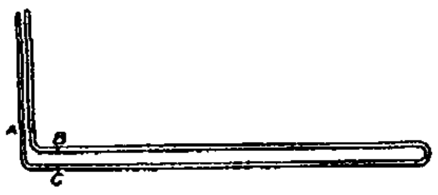

Fig. 1

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[1] *Zeit. phys. Chem.*, 75, 245 (1910).

[2] Kristallisieren und Schmelzen, p. 148 (1903).

tube so that there was a layer about an inch deep on the surface of the water. The tube was then placed through an opening in the cover of the thermostat described in the paper preceding this, and allowed to come to the temperature of the bath. This took at least three minutes. At the end of this time crystallization was started in the tube by scratching the side of the tube just below the layer of oil by means of a piece of wire. The time necessary for the crystalline surface to travel from B to C (1 meter in distance) was measured with a stop watch. Several measurements were made with the same tube full of water, and it was found that this gave just the same results as were obtained by filling the tubes each time an experiment was carried out. Results obtained by using tubes in which the water had been standing for several weeks, however, diverged greatly from those obtained with freshly filled tubes. This was doubtless due to the glass dissolved by the water on standing.

An unsuccessful attempt was made to measure the velocity of crystallization in tubes with very thin walls. Spontaneous crystallization occurred much more frequently than with thick-walled tubes that permitted the water to cool slowly. The tubes used in the first experiments had a bore of 7 mm and an outside diameter of 12 mm. The velocity of crystallization was measured to —9°. Below this temperature the results were uncertain, owing to spontaneous crystallization taking place before the tube was cooled to the temperature of the bath. The results obtained are given in Table II and shown graphically in Fig. 2, Curve I, in which the velocity is expressed as centimeters per minute. Experiments with tubes of different bores and different thickness of walls were carried out for the purpose of showing the influence of these factors on the speed of crystallization of water. Tables III and IV give the diameter of the tube and the results obtained. These results are also shown graphically in Fig. 2, Curves II and III.

Tammann has shown that for undercooled liquids the velocity of crystallization increases with the degree of undercooling until a maximum is reached below which temperature

TABLE II (CURVE I)

Velocity of crystallization of water
Outside diameter of tube 12 mm
Inside diameter of tube 7 mm

Temp.	Time for 1 meter	Average	Velocity of linear crystallization cm per minute
—2.00	194.0	190.0	31.6
	186.0		
—3.61	124.4		
	124.7		
	123.2		
	122.1		
	127.0		
	127.2		
	122.0	124.0	48.4
—4.67	85.0		
	86.3		
	83.0		
	85.1		
	82.6		
	82.5		
	85.2	84.2	71.4
—5.86	56.1		
	54.0		
	53.9		
	56.8		
	57.0		
	57.0		
	57.0	56.0	107.1
—6.18	53.1		
	51.4	52.3	114.7
—7.10	22.0		
	23.0		
	22.5	22.5	266.7
—7.50	19.0		
	19.9	19.45	308.0
—8.19	14.6		
	14.3	14.45	415.2
—8.38	12.0		
	10.3		
	11.5		
	12.7		
	12.0	11.7	513.0
—9.07	8.8		
	8.8		
	8.7	8.77	684.0

there is, at least for several degrees, no relation between the speed of crystallization and the temperature of the bath. Continued cooling of the bath results in decreasing the speed of crystallization. This phenomenon is explained as follows: At temperatures in the neighborhood of the freezing point of the solution, the velocity of crystallization is retarded by the heat of crystallization, which heats the layer of liquid that is in contact with the growing crystalline surface. The velocity with which this layer is cooled by the outside bath is one of the factors in determining the speed of crystallization. The greater the number of degrees the liquid is undercooled, the more quickly will this layer take on the temperature of the outside bath, consequently the less will the effect of the heat of crystallization be felt. This will result in the speed of crystallization increasing with the undercooling, up to a point at which the above effect will just neutralize the heat of crystallization. The layer will then have the temperature of the melting point of the substance, and this point will be the maximum velocity of crystallization.

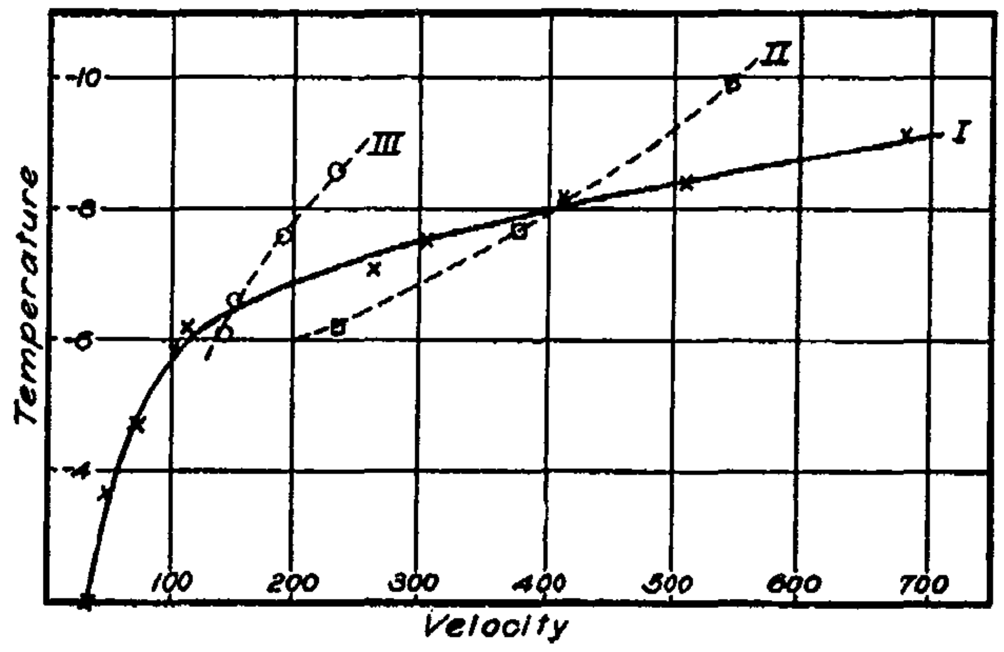

Fig. 2

From the above consideration it is evident that the size of the bore and the thickness of the walls of the crystallizing tubes are important factors in the velocity of crystallization,

TABLE III (CURVE II)

Velocity of crystallization of water
Outside diameter of tube 14 mm
Inside diameter of tube 11 mm

Temp.	Time for 1 meter	Average	Velocity of linear crystallization cm per minute
—6.17	24.7		
	26.7		
	25.5		
	25.1		
	25.3	25.5	235.3
—7.65	16.4		
	16.0		
	15.35		
	15.70	15.9	377.8
—9.92	9.85		
	12.50		
	10.90		
	10.50	10.94	548.4

TABLE IV (CURVE III)

Velocity of crystallization of water
Outside diameter of tube 10 mm
Inside diameter of tube 3.5 mm

Temp.	Time for 1 meter	Average	Velocity of linear crystallization cm per minute
—6.10	41.6		
	42.1		
	41.4		
	42.0		
	41.5	41.7	144.0
—6.60	39.5		
	40.7		
	39.1		
	38.1	39.6	151.5
—7.58	31.0		
	31.0		
	30.8		
	31.1	31.0	193.5
—8.58	25.9		
	26.0		
	25.0	25.6	234.4

inasmuch as they determine the rate of the cooling of the crystallizing liquid. The results obtained in these experiments, using tubes of different diameters, is thus explained. This does not, however, explain the fact that at —6° the undercooled water represented by Curve III crystallizes faster than that in tube I, while at —8° the reverse is true.

An inspection of Curve I shows that the point of maximum crystallization lies below the temperatures at which these experiments were carried out. Many attempts were made to determine the velocity of crystallization at —15°, but the liquid always crystallized spontaneously before the tube was cooled to the temperature of the bath. Crystallizing tubes were prepared by filling with pure boiling water, evacuating, and then sealing, but they could not be undercooled any lower than those prepared in the manner already described.

These experiments are being continued, the particular line of investigation being the effect of dissolved substances upon the velocity of crystallization of water.

Summary

1. The linear velocity of crystallization of undercooled water has been determined to —9°.

2. The thickness of the wall of the tube used in these determinations is an important factor in determining the speed of crystallization.

3. Because of spontaneous crystallization it was impossible to determine the temperature of the maximum velocity of crystallization of water.

Department of Chemistry
University of Wisconsin

ELECTROMOTIVE FORCES AND ELECTRODE POTENTIALS IN MIXED SOLVENTS

BY J. N. PEARCE AND W. H. FARR

The subject of electromotive forces in non-aqueous solvents was first studied by Jones.[1] He measured the electromotive force of a number of cells of the type:

$$Ag—AgNO_3.aq.—AgNO_3.alc.—Ag,$$

using the same concentration of silver nitrate in the two solvents. His original idea was to determine by this method the degree of dissociation of the silver nitrate in the second solvent, assuming that the solution tension of silver in alcohol is the same as it is in water. He soon found that the solution tension of a metal is not the same for all solvents, but has a distinct characteristic value for every solvent. Using the values for the dissociation of silver nitrate in alcohol found by Völlmer,[2] he found the ratio between the solution tension of silver in water and in ethyl alcohol to be between 0.021 and 0.024, which would indicate that the solution tension of silver in the alcohol is approximately 40 times smaller than the value obtained in water. Owing to the uncertainty as to the degree of dissociation of silver nitrate in methyl alcohol, he was unable to compute the value of the solution tension of silver in that solvent. In all of the above measurements the alcoholic solutions were positive with respect to the water solutions.

Jones and Smith[3] measured the electromotive force of the cell,

$$Zn—ZnCl_2.aq.—ZnCl_2.alc.—Zn,$$

and, using the values for the dissociation of zinc chloride in ethyl alcoholic solutions found by the boiling-point method, calculated the solution tension of zinc in ethyl alcohol to be

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[1] Zeit. phys. Chem., 14, 346 (1894).

[2] Dissertation, Halle, 1892.

[3] Am. Chem. Jour., 23, 379 (1900).

between 1.9 × 10^{10} and 2.7 × 10^{10}, a value approximately 10^8 times smaller than the value in pure water.

Campetti[1] determined the electromotive forces produced between alcoholic and aqueous solutions of the chlorides of ammonium, lithium, calcium, copper, zinc and cadmium and the iodides of zinc and cadmium. He also found that the alcoholic solutions are positive with respect to the aqueous solutions, but made no attempt to calculate the solution tensions.

Kahlenberg[2] measured the electrode potentials of a large number of metals in various organic solvents, using 0.10 *N* solutions of their salts whenever possible, and found that the solution tension of a metal varies widely with the nature of the solvent. He expresses his conclusions in the following words: "If the electrolytic solution tension theory be held at all, there seems to be no escape from the conclusion that the solution tension varies for different solvents and mixtures of solvents. If the solution tension changes not only with the solvent, but also with the nature of the dissolved substance present, it is questionable, to say the least, whether the hypothesis of an electrolytic solution tension is helpful at all." He also tested and found that Faraday's laws hold for non-aqueous solutions.

The first measurements of the electromotive forces of concentration cells in alcoholic solutions were made by Wilson.[3] His cells contained silver nitrate dissolved in methyl and ethyl alcohol and the measurements were made at 0° and 25°. From the agreement between his results and the values calculated from the conductivities of the solutions he draws the conclusion that the Nernst equation can also be applied to non-aqueous solutions, yet admitting at the same time that the Nernst formula can hardly be recognized as giving more than approximate values.

Getman[4] and Getman and Gibbons[5] have attempted to

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[1] Atti Accad. Torino, 29, 61, 228 (1893).

[2] Jour. Phys. Chem., 3, 379 (1899).

[3] Am. Chem. Jour., 35, 78 (1906).

[4] Ibid., 46, 117 (1911).

[5] Ibid., 48, 124 (1912).

measure the solution tensions of cadmium and zinc in alcoholic solutions of their chlorides. Since it is impossible to determine the degree of dissociation of these salts in these alcohols, they were unable to calculate the solution tensions of these metals. In working with the zinc electrode they state that their results were neither uniform nor capable of duplication.

Neustadt and Abegg[1] investigated a number of cells containing $Pb(ClO_3)_2$, $CuCl_2$, $CdCl_2$, $ZnCl_2$, $Hg(NO_3)_2$ and $AgNO_3$, with the corresponding metals as electrodes, the solvents used being water, methyl alcohol, ethyl alcohol, acetone and pyridine. They found, as have other investigators, that the electromotive forces vary with the nature of the solvent. They also made a study of the liquid potentials between solutions in the different solvents. Some of the cells used were in the form of chains containing as high as three different intermediate solvents. The total electromotive force is the algebraic sum of all the liquid potentials and the electrode potentials in the chain. This difference in potential at the contact of the two solutions can be reduced to a negligible quantity in the case of similar end solutions, by interposing between them a solution of an indifferent electrolyte in a second solvent. Obviously the total electromotive force at the junction of the solutions becomes zero when the two opposing liquid potentials are equal.

Thus far very little work has been done on the effect of mixed solvents on electromotive forces. Starting with a given alcoholic solution of silver nitrate, Jones[2] determined the effect of successive replacement of the alcohol by water upon the electromotive force, keeping the concentration of the silver nitrate constant throughout. The greatest change was obtained with first additions of water, the effect becoming less and less as the percentage of water increases. Similar results were obtained by Kahlenberg[2] for mixtures of pyridine and water.

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[1] Zeit. phys. Chem., 69, 486 (1910).

[2] Loc. cit.

It has been frequently observed that the properties of mixtures of ethyl and methyl alcohol and their solutions obey closely the law of mixtures. On the other hand, binary mixtures of water and ethyl or methyl alcohol show for the most part either a pronounced maximum or minimum with respect to the properties considered, indicating changes in the properties of the solvent due to the mutual effect of the two solvents upon each other. Somewhat similar relations, as we shall see, have been found for the electromotive forces and electrode potentials in these solvents and their mixtures.

With the hope that further light might be thrown on the electrochemistry of solutions the present investigation was undertaken, the object being to study the effect of the nature of the solvent, the concentration and the temperature on the electrode potentials and electromotive forces of cells in water, ethyl alcohol, methyl alcohol and in the binary mixtures of these solvents.

Materials and Solutions

Water.—The conductivity water used was prepared according to the method of Jones and Mackay.[1] It had a specific conductance of approximately 1.5×10^{-6} mhos.

Ethyl Alcohol.—Ordinary 95% alcohol which had been allowed to stand over fresh quicklime, or refluxed with quicklime for ten or twelve hours, was first distilled, the distillate allowed to stand over anhydrous copper sulphate for three weeks and then redistilled. The middle portion of this distillate was then refluxed with metallic calcium for several hours and again distilled. Finally, it was refluxed for a short time with a little pure silver nitrate and then distilled into dry glass-stoppered bottles which were kept in a dark cool place. In each distillation only that portion passing over at 78.3° ± 0.1 was collected. The treatment with silver nitrate was found to be absolutely necessary, since otherwise the silver nitrate solutions in ethyl alcohol undergo rapid reduction.

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[1] Am. Chem. Jour., 19, 83 (1897).

Solutions made up with alcohol thus prepared keep indefinitely without any apparent trace of reduction.

Methyl Alcohol.—Kahlbaum's best grade of methyl alcohol was further purified in the same manner as the ethyl alcohol except that the treatment with quicklime was omitted. In each distillation only that portion was collected which passed over at 60° ± 0.1.

The binary mixtures of the three solvents were made up on a percentage basis by direct weighing and the weights of each solvent are accurate to ±0.1 gram per liter.

Silver Nitrate.[1]—Chemically pure silver nitrate was recrystallized by the rapid cooling of a hot saturated solution of the salt in conductivity water. The fine colorless crystals were then transferred to a Büchner funnel, washed with ice-cold conductivity water, sucked dry and subsequently heated for several hours in a toluol bath at 109°. The pure dry salt was preserved in dark bottles and handled with as little exposure to light as possible.

Potassium Chloride.—Chemically pure potassium chloride was further purified by reprecipitation from a saturated solution by means of pure hydrogen chloride gas. The precipitate was then filtered on a Büchner funnel, washed with conductivity water and finally heated to dryness in an air-bath.

Solutions.—All solutions were prepared by direct weighing, or by the dilution of a freshly prepared solution of higher concentration, the solution being made up to volume at 25°. Special care was taken to avoid exposure of the solutions to the light.

Apparatus

The battery, consisting of six half-cells and two calomel electrodes, was especially designed for this work. Each half-cell was provided with a stop-cock in the side-tube which could be kept closed except while readings were being made, thus preventing unnecessary diffusion between the solutions. As a further precaution a loose plug of filter paper was inserted

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[1] Kahlbaum's C. P. salt was used.

in the end of the tube after filling and this to a large extent prevented diffusion even when the stop-cocks were open. The intermediate vessel was a glass tube ten inches long and one inch in diameter and was provided with eight upright tubules into which the side-tubes of the half-cells were inserted through tight-fitting, one-hole rubber stoppers. This arrangement possessed the double advantage that the whole formed a closed system and that the whole number of cells could be set up and a complete series of readings made without changing anything except the stop-cocks and contacts. In order to eliminate the diffusion potential between the solutions the intermediate trough was filled with a normal solution of pure ammonium nitrate. It was assumed that this solution entirely eliminated the diffusion potential.[1]

The calomel cells were made up according to the method described by Loomis and Acree.[2] Pure mercurous chloride was repeatedly shaken with a 0.10 *N* solution of potassium chloride and a little pure mercury, allowed to settle, and the supernatant liquid decanted. A fresh portion of the potassium chloride solution was then shaken with the calomel until thoroughly saturated. In the bottom of the electrode vessel was first placed a small quantity of pure mercury and over this a layer of the prepared calomel paste and the cell filled with the solution of potassium chloride which had been saturated with mercurous chloride. The single potential of the calomel electrode was calculated from the value given by Richards,[3] the values obtained being +0.5986 at 0° and +0.6186 at 25°. The calomel electrodes were renewed alternately every two weeks and were found to be reproducible to within ±0.30 millivolt.

The measurements of the electromotive forces were made with a Wolff potentiometer in connection with a Leeds-Northrup "Type H" wall galvanometer. Differences of potential as small as 0.01 millivolt could easily be detected

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[1] Ostwald-Luther: Messungen, 3rd. Ed., p. 448.

[2] Am. Chem. Jour., 46, 585 (1911).

[3] Zeit. phys. Chem., 24, 39 (1897).

in aqueous solutions, but owing to the high resistance of most of the alcoholic solutions it was not possible to read closer than 0.1 millivolt. A certified Clark cell having an electromotive force of 1.42445 volts was used as the standard; the working battery was a single lead accumulator which had been charged some time previously and consequently its voltage was very constant.

The constant temperature baths were designed especially for this work and were of sufficient size to accommodate the whole battery of cells. Both consisted of a large metal box within a larger wooden box, the intervening space being filled with insulating material. The water in the 25°-bath was kept in rapid circulation, electrically heated and the temperature kept at 25° ± 0.01 by means of an electrically controlled regulator. The 0°-bath consisted of clean, finely crushed ice moistened with distilled water. Both baths were provided with covers and arrangements made whereby readings could be taken even while the baths were closed. Only certified thermometers which permitted reading to 0.01° were used.

Previous investigators have reported considerable difficulty in obtaining constant easily producible electrodes. A large amount of work had to be done, therefore, before a satisfactory method was found for preparing the silver electrodes. For the first electrodes a short piece of pure silver wire to which had been soldered a small copper wire was sealed into a narrow glass tube by means of fused silver chloride, leaving about a half-inch of the silver wire exposed. To prevent amalgamation of the silver by the mercury which was used for making contact with the copper wire, the tube was filled well above the junction with melted paraffin. Before using, all the electrodes were plated in a solution of potassium silver cyanide. To insure uniform plating they were connected in series and a small current of 10 milliamperes passed for ten or twelve hours. Pure silver wires were used as anodes. After plating the electrodes were quickly removed, rinsed with distilled water and allowed to stand for twenty-four hours in contact with a plate of pure silver immersed in a silver nitrate solution. Regardless of these precautions, the electrode potentials varied widely and frequently by as much as ±5 millivolts. Also, for a given electrode, the potential gradually changes with the time. The accompanying decrease is most rapid at first, then more slowly, and finally attains a constant value after fifteen or twenty minutes. Upon examination of the electrodes it was found that the fused silver chloride had become disintegrated and partially removed. This difficulty was overcome by sealing the silver wire directly into the glass tube by means of soft sealing glass. That the nature of the surface of the electrode has a considerable influence was shown by the fact that satisfactory agreement between the different electrodes is obtained only when the electrode surfaces are smooth.

The following table will serve to illustrate how easily the electrode potentials can be duplicated. The two sets of readings represent the electromotive force of silver in 0.05 *N* silver nitrate in ethyl alcohol against the 0.01 *N* calomel electrode at 25°. The readings were taken at different times, with different solutions and with different electrodes.

Time	Electrodes	E. M. F. Volts
Jan. 14, 1914	A	0.4502
	B	0.4502
	C	0.4505
	D	0.4503
		Mean, 0.4503
Mar. 19, 1914	G	0.4506
	J	0.4503
	O	0.4500
	U	0.4505
		Mean, 0.45035

Before using, the electrodes were checked against each other and five were chosen for each concentration series.

one reading being taken with each electrode in each solution. After using, the electrodes were thoroughly rinsed with pure alcohol and dried before being inserted into the next cell. Each voltage given in the following tables is, therefore, the mean of five different determinations.

Theoretical

The total electromotive force of a battery is the sum of four potential differences, viz., at the junction of the connecting wires with the two electrodes, at the surfaces of contact between the electrodes and their respective solutions, and at the junction of the two solutions. Under ordinary conditions the first potential difference in concentration cells is absent.

According to the osmotic theory of the cell as established by Nernst the difference of potential between a metal and a solution of one of its salts is given by the relation,

$$\pi = \frac{RT}{nf} \log_e \frac{P}{p}, \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where R represents the gas constant (2 cal.), T the absolute temperature, *n* the valence of the cation, *f* one Faraday (96540 coulombs), P the solution tension of the metal, and *p* the osmotic pressure of the metallic ions in the solution. The electromotive force at the junction of the two solutions is given by the relation,

$$\pi = \frac{u - v}{u + v} \cdot \frac{RT}{nf} \log_e \frac{p_2}{p_1} \ldots\ldots\ldots\ldots\ldots (2)$$

where *u* and *v* represent the speeds of the cation and anion, respectively. When two electrodes of the same metal dip into solutions of different concentrations of its ions the resulting electromotive force is the algebraic sum of the electrode potentials and the diffusion potential, or

$$\pi = (\pi_1 - \pi_2) - \pi_3 = \frac{RT}{nf} \log_e \frac{p_2}{p_1} - \frac{u - v}{u + v} \cdot \frac{RT}{nf} \log_e \frac{p_2}{p_1}, \text{ or}$$

from which we obtain by rearrangement of terms,

$$\pi = \frac{2v}{u + v} \cdot \frac{RT}{nf} \log_e \frac{p_2}{p_1} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The electromotive force is therefore proportional to the logarithm of the ratio of the osmotic pressures of the metallic ions in the two solutions and is independent of their absolute magnitudes. Since the osmotic pressure of the ions in a given solution is proportional to the ionic concentration, which in turn is dependent upon the degree of dissociation, and since the degree of dissociation may be considered as being proportional to the molecular conductivity, we may write,

$$\frac{p_2}{p_1} = \frac{\alpha_2 c_2}{\alpha_1 c_1} = \frac{\lambda_2 c_2}{\lambda_1 c_1} \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where p_1 and p_2 represent the osmotic pressures of the cations, α_1 and α_2 the degrees of dissociation, and λ_1 and λ_2 the equivalent molecular conductivities of the two solutions whose concentrations are c_1 and c_2, respectively. By substitution in (3) we have

$$\pi = \frac{2v}{u+v} \cdot \frac{RT}{nf} \log_e \frac{\lambda_2 c_2}{\lambda_1 c_1} \ldots\ldots\ldots\ldots\ldots (5)$$

In this work the diffusion potential is assumed to be completely eliminated by the interposition of the ammonium nitrate solution. Hence by substituting (4) in

$$\pi = (\pi_1 - \pi_2) = \frac{RT}{nf} \log_e \frac{p_2}{p_1} \ldots\ldots\ldots\ldots (6)$$

which represents the electromotive force of the cell due to the potential differences at the two electrodes, we have

$$\pi = \frac{RT}{nf} \log_e \frac{\lambda_2 c_2}{\lambda_1 c_1} \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

The value of P, the solution tension of the metal, can be calculated as follows. From Equation 1 we obtain the transformation

$$\log_e P = \frac{\pi n f}{RT} + \log_e p \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

The osmotic pressure of the ions is given by the relation

$$p = 22.4\, c\, \alpha \frac{T}{273}.$$

The term $\frac{\lambda_v}{\lambda_\infty}$ may be substituted for α, which gives as the complete expression for P,

$$\log_e P = \frac{\pi n f}{RT} + \log_e\left(22.4\, c\, \frac{\lambda_v}{\lambda_\infty}\, \frac{T}{273}\right) \dots\dots\dots (9)$$

The temperature coefficients of the electrode potentials were calculated by means of the equation,

$$\frac{d\pi}{dt} = \frac{\pi_0 - \pi_{25}}{\pi_0 \cdot 25}$$

The relation between the electrical and chemical energies in a cell is given by the Helmholtz equation,

$$\pi = \frac{Q}{f} + T\frac{d\pi}{dt} \dots\dots\dots\dots\dots\dots (10)$$

where Q is the heat of ionization of the metal in calories. By transposition we obtain

$$Q = f\left(\pi - T\frac{d\pi}{dt}\right) \dots\dots\dots\dots\dots\dots (11)$$

which is the equation used for calculating the heats of ionization.

Results

In Tables I to X are given the results obtained for solutions in ethyl and methyl alcohols and their binary mixtures.

Table I

Electrode potentials in ethyl and methyl alcohol

25°

N	100 ethyl Volts	75 ethyl 25 methyl Volts	50 ethyl 50 methyl Volts	25 ethyl 75 methyl Volts	100 methyl Volts
0.10	1.0752	1.0795	1.0836	1.0868	1.0960
0.05	1.0689	1.0740	1.0778	1.0808	1.0841
0.025	1.0574	1.0612	1.0659	1.0680	1.0708
0.01	1.0412	1.0456	1.0491	1.0543	1.0612
0.005	1.0229	1.0273	1.0323	1.0374	1.0425

TABLE II

0°

N	100 ethyl Volts	75 ethyl 25 methyl Volts	50 ethyl 50 methyl Volts	25 ethyl 75 methyl Volts	100 methyl Volts
0.10	1.0745	1.0778	1.0794	1.0824	1.0868
0.05	1.0676	1.0719	1.0734	1.0778	1.0810
0.025	1.0526.	1.0579	1.0623	1.0662	1.0684
0.01	1.0307	1.0338	1.0393	1.0438	1.0506
0.005	1.0118	1.0160	1.0256	1.0315	1.0374

TABLE III

Temperature coefficients of electrode potentials of silver in ethyl and methyl alcohol

N	100 ethyl	75 ethyl 25 methyl	50 ethyl 50 methyl	25 ethyl 75 methyl	100 methyl
0.10	+0.000026	+0.000063	+0.000156	+0.000156	+0.000341
0.05	0.000048	0.000078	0.000166	0.000109	0.000115
0.025	0.000182	0.000126	0.000136	0.000068	0.000090
0.01	0.000420	0.000458	0.000377	0.000403	0.000404
0.005	0.000448	0.000445	0.000272	0.000268	0.000198

The alcoholic solutions are in all cases positive with respect to the calomel electrode. The single potentials in methyl alcohol are higher than those in ethyl alcohol, which is in harmony with the results obtained by Jones.[1] It is interesting to note that the curve showing the effect of the mixtures of the alcohols on the electrode potentials are practically straight lines (Figs. I and II). For all these solvents the electrode potentials decrease with increase in dilution, *i. e.*, the electrode becomes less and less positive to the solution (Figs. III and IV).

Kahlenberg[1] found the single potentials of silver in a 0.10 *N* solution of silver nitrate in ethyl and methyl alcohol to be 1.083 and 1.108 volts, respectively, while the values here obtained for the corresponding solutions are 1.0732 and

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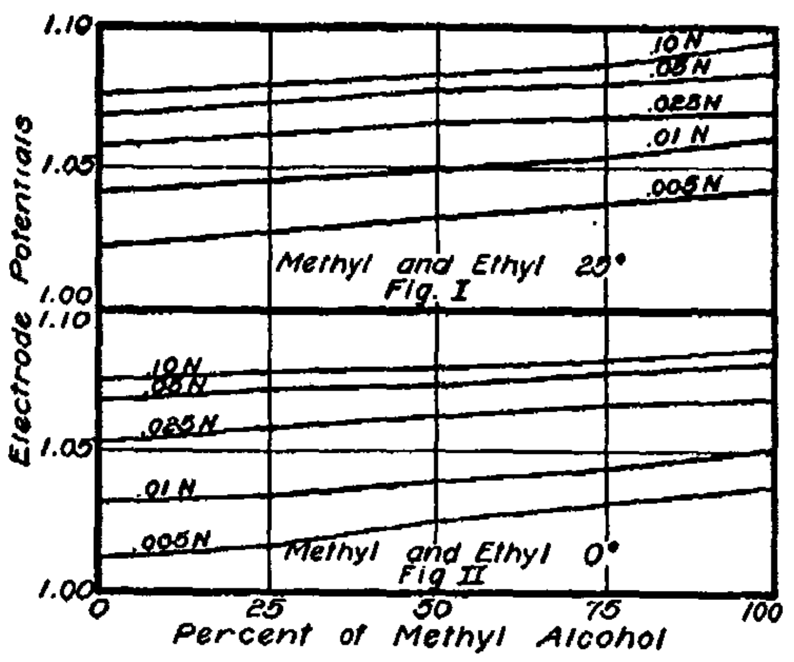
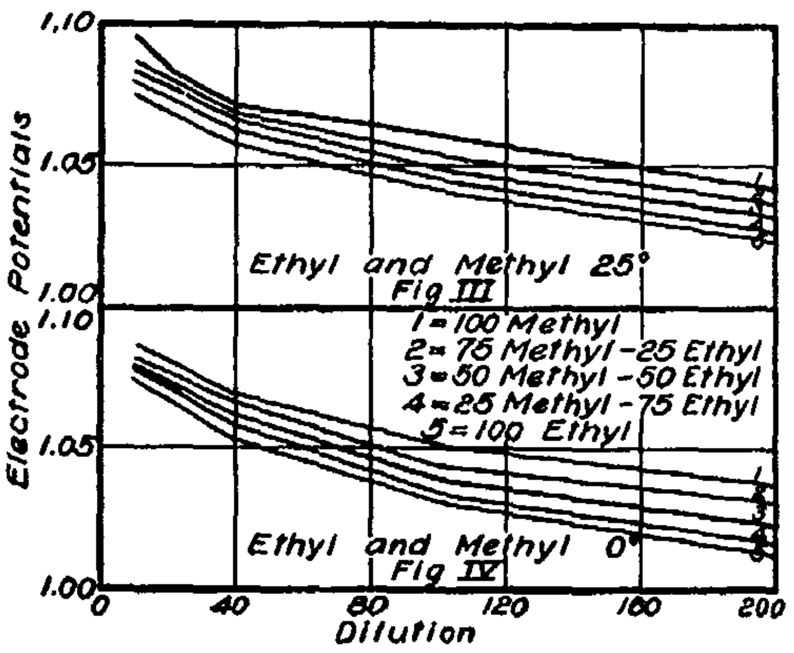
[1] Loc. cit.

1.0960 volts. The agreement may be considered satisfactory since Kahlenberg did not take any special precautions in preparing his electrodes nor does he claim that his results are more than qualitative in nature.





The electrode potentials of the alcoholic solutions increase slightly with rise in temperature between 0° and 25°. The amount of this increase is small and therefore the positive temperature coefficients are hardly more than approximate values. Except in the solutions in the pure methyl alcohol, the temperature coefficients increase with increase in dilution, the increase being most marked on the ethyl alcohol side.

A few measurements were made on cells of the type

$$Ag — AgNO_3 \text{ (ethyl)} — AgNO_3 \text{ (methyl)} — Ag,$$

both solutions having exactly the same concentration. In these cells the solutions in methyl alcohol are always positive to those in ethyl alcohol, as was found by Jones, but the electromotive forces of the cells are in all cases considerably larger than those obtained by him. The results of these measurements at 25° are given in the following table:

TABLE IV

Concentration cells in two alcohols

N	E. M. F. Volts
0.10	0.0215
0.05	0.0200
0.025	0.0210
0.01	0.0210
0.005	0.0210

It will be observed that using the two solvents the electromotive forces in these cells are independent of the concentration used. If, as has been assumed, the electromotive force at the junction of the two solutions has been entirely eliminated and since the electromotive force of a concentration cell at a given temperature is proportional to the logarithm of the ratio of the ionic concentrations in the two solutions, it follows that the ratio between the ionic concentrations for equivalent concentrations of the salt in the two alcohols is constant and independent of the dilution.

The electromotive forces of all the possible concentration cells for each solvent have been determined and they are given in Tables V and VI:

TABLE V

Concentration cells in ethyl and methyl alcohol

25°

N_1-N_2	100 ethyl Volts	75 ethyl 25 methyl Volts	50 ethyl 50 methyl Volts	25 ethyl 75 methyl Volts	100 methyl Volts
0.1 -0.05	0.007	0.004	0.006	0.006	0.012
0.1 -0.025	0.025	0.019	0.023	0.018	0.024
0.1 -0.01	0.034	0.035	0.038	0.039	0.040
0.1 -0.005	0.054	0.052	0.054	0.051	0.058
0.05 -0.025	0.011	0.012	0.012	0.013	0.012
0.05 -0.01	0.039	0.029	0.029	0.029	0.031
0.05 -0.005	0.045	0.046	0.044	0.044	0.047
0.025-0.01	0.014	0.020	0.016	0.017	0.022
0.025-0.005	0.034	0.033	0.032	0.032	0.038
0.01 -0.005	0.019	0.015	0.015	0.012	0.016

TABLE VI

0°

N_1-N_2	100 ethyl Volts	75 ethyl 25 methyl Volts	50 ethyl 50 methyl Volts	25 ethyl 75 methyl Volts	100 methyl Volts
0.1 -0.05	0.007	0.008	0.009	0.008	0.011
0.1 -0.025	0.022	0.024	0.022	0.018	0.019
0.1 -0.01	0.044	0.044	0.041	0.037	0.039
0.1 -0.005	0.062	0.060	0.051	0.050	0.051
0.05 -0.025	0.015	0.014	0.010	0.011	0.012
0.05 -0.01	0.038	0.037	0.033	0.033	0.033
0.05 -0.005	0.055	0.047	0.046	0.044	0.043
0.025-0.01	0.022	0.024	0.020	0.020	0.018
0.025-0.005	0.040	0.032	0.035	0.033	0.032
0.01 -0.005	0.017	0.016	0.014	0.013	0.013

The values of the electromotive forces of these cells, calculated by means of Equation 5 from the conductivity values of the corresponding silver nitrate solutions, are given in Tables VII and VIII. For the benefit of other workers in this field the conductivity data are added in Tables IX and X.

TABLE VII

25°

N_1-N_2	100 ethyl Volts	75 ethyl 25 methyl Volts	50 ethyl 50 methyl Volts	25 ethyl 75 methyl Volts	100 methyl Volts
0.1 -0.05	0.012	0.012	0.011	0.012	0.012
0.1 -0.025	0.024	0.024	0.025	0.026	0.024
0.1 -0.01	0.047	0.044	0.044	0.044	0.046
0.1 -0.005	0.061	0.059	0.059	0.057	0.060
0.05 -0.025	0.012	0.012	0.013	0.014	0.011
0.05 -0.01	0.035	0.033	0.032	0.032	0.033
0.05 -0.005	0.049	0.047	0.047	0.045	0.048
0.025-0.01	0.022	0.020	0.019	0.017	0.022
0.025-0.005	0.038	0.034	0.034	0.031	0.037
0.01 -0.005	0.014	0.014	0.015	0.013	0.015

TABLE VIII

0°

N_1-N_2	100 ethyl Volts	75 ethyl 25 methyl Volts	50 ethyl 50 methyl Volts	25 ethyl 75 methyl Volts	100 methyl Volts
0.1 -0.05	0.012	0.011	0.011	0.012	0.012
0.1 -0.025	0.025	0.024	0.025	0.026	0.023
0.1 -0.01	0.046	0.044	0.044	0.044	0.046
0.1 -0.005	0.061	0.060	0.059	0.058	0.061
0.05 -0.025	0.012	0.013	0.013	0.013	0.011
0.05 -0.01	0.034	0.033	0.032	0.033	0.034
0.05 -0.005	0.048	0.047	0.047	0.046	0.049
0.025-0.01	0.022	0.020	0.020	0.019	0.022
0.025-0.005	0.032	0.034	0.034	0.032	0.037
0.01 -0.005	0.014	0.015	0.015	0.013	0.014

In all the above concentration cells the most concentrated solution is, as we should expect, positive with respect to the more dilute. It should be borne in mind that the high resistances encountered in these solutions make the measurement of the electromotive force somewhat difficult and more or less subject to error. Nevertheless the agreement between the calculated and observed electromotive forces may be considered very satisfactory and shows without question that the Nernst formula can be applied not only to non-aqueous solvents, but also to binary mixtures of these solvents.

TABLE IX

Molecular conductivities of silver nitrate[1]

25°

N	100 ethyl	75 ethyl 25 methyl	50 ethyl 50 methyl	25 ethyl 75 methyl	100 methyl
0.10	13.215	18.021	23.670	30.214	38.575
0.05	16.380	22.604	29.952	37.548	47.919
0.025	20.180	27.479	35.548	43.314	61.361
0.01	21.050	31.890	42.390	54.090	64.800
0.005	42.520	36.410	47.290	64.400	72.810

TABLE X

0°

N	100 ethyl	75 ethyl 25 methyl	50 ethyl 50 methyl	25 ethyl 75 methyl	100 methyl
0.10	8.246	11.770	16.154	21.506	28.122
0.05	10.253	14.821	20.404	26.788	35.142
0.025	12.611	17.905	24.094	31.580	45.061
0.01	13.610	29.780	29.040	38.010	46.730
0.005	15.610	23.400	32.17	44.940	52.490

In Tables XI and XII are given the results obtained for solutions in water and ethyl alcohol and in their binary mixtures.

TABLE XI

Electrode potentials of silver in water and ethyl alcohol

25°

N	100 water Volts	75 water 25 ethyl Volts	50 water 50 ethyl Volts	25 water 75 ethyl Volts	100 ethyl Volts
0.10	1.0098	1.0136	1.0275	1.0442	1.0758
0.05	0.9971	1.0044	1.0152	1.0340	1.0690
0.025	0.9809	0.9891	1.0002	1.0198	1.0584
0.0125	0.9704	0.9783	0.9892	1.0047	1.0498
0.00625	0.9557	0.9644	0.9746	0.9908	1.0372

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[1] The conductivity values of the *0.01 N* and *0.005 N* are taken from the work of Jones and Rouiller (Am. Chem. Jour., 36, 427 (1906)). The remaining values were determined in this laboratory.

TABLE XII

0°

N	100 water Volts	75 water 25 ethyl Volts	50 water 50 ethyl Volts	25 water 75 ethyl Volts	100 ethyl Volts
0.10	1.0108	1.0162	1.0222	1.0336	1.0742
0.05	0.9995	1.0061	1.0132	1.0238	1.0676
0.025	0.9866	0.9940	1.0022	1.0130	1.0525
0.0125	0.9780	0.9838	0.9933	1.0020	1.0379
0.00625	0.9651	0.9716	0.9822	0.9920	1.0242

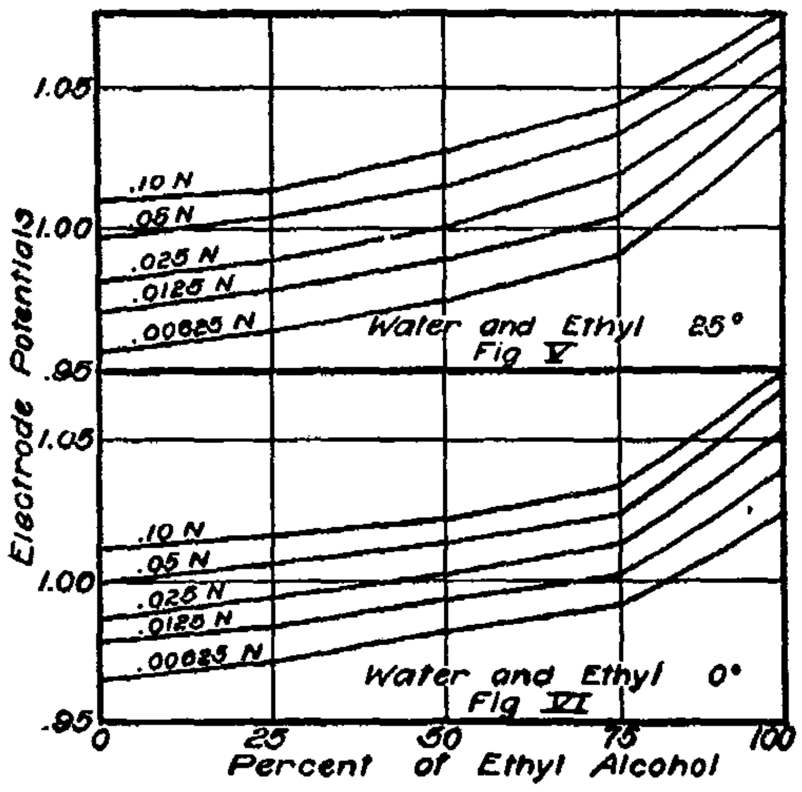
TABLE XIII

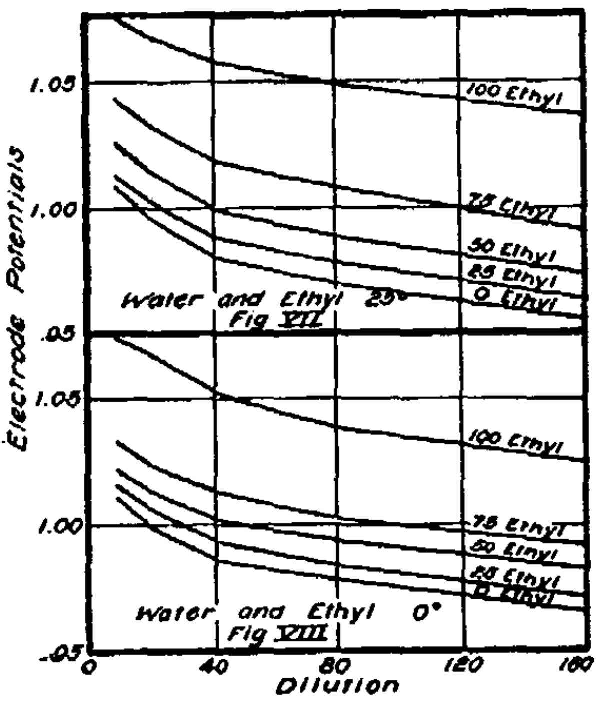
Temperature coefficients of electrode potentials of silver in water and ethyl alcohol

N	100 water	75 water 25 ethyl	50 water 50 ethyl	25 water 75 ethyl	100 ethyl
0.10	—0.000039	—0.000103	+0.000208	+0.000415	+0.000048
0.05	—0.000100	—0.000088	+0.000100	+0.000400	+0.000053
0.025	—0.000231	—0.000198	—0.000080	+0.000269	+0.000244
0.0125	—0.000311	—0.000225	—0.000165	+0.000108	+0.000458
0.00625	—0.000390	—0.000297	—0.000310	—0.000047	+0.000507

The electrode potentials of silver are somewhat smaller in the aqueous solutions than they are in the ethyl alcohol. The effect of change of solvent on the electrode potentials is shown in Figs. V and VI. Starting with an alcoholic solution, the decrease in potential is most rapid for the first additions of water, the decrease becoming less and less for each subsequent addition. As we should expect, the electrode potential of silver in water solutions decreases with increasing dilution and the rate of this decrease is approximately the same as was found in the alcoholic solutions (see Figs. VII and VIII).

Contrary to the behavior observed in the alcoholic solutions, the electrode potential decreases with rise in temperature between 0° and 25°. Negative temperature coefficients are found not only in the pure water and the 75 percent water mixture, but also in the more dilute solutions of the remaining binary solvents. It is to be observed that the influence due to the water in these mixtures is displaced toward higher dilutions as the percentage of the alcohol increases. Except in the pure ethyl alcohol, the temperature coefficients of the electrode potentials decrease with increasing dilution.





The electromotive forces of the concentration cells in water and ethyl alcohol and their mixtures are given in Tables XIV and XV. The values of the electromotive forces of these cells as calculated from the conductivity data (Tables XVIII and XIX) are given in Tables XVI and XVII. The agreement between the calculated and observed values is very satisfactory.

TABLE XIV

25°

Concentration cells in water and ethyl alcohol

N_1-N_2	100 water Volts	75 water 25 ethyl Volts	50 water 50 ethyl Volts	25 water 75 ethyl Volts	100 ethyl Volts
0.1 –0.05	0.015	0.015	0.015	0.015	0.012
0.1 –0.025	0.032	0.031	0.032	0.029	0.025
0.1 –0.0125	0.045	0.044	0.049	0.046	0.035
0.1 –0.00625	0.062	0.060	0.060	0.060	0.049
0.05 –0.025	0.016	0.016	0.016	0.014	0.012
0.05 –0.0125	0.031	0.032	0.032	0.031	0.025
0.05 –0.00625	0.048	0.049	0.046	0.045	0.040
0.025 –0.0125	0.016	0.016	0.015	0.014	0.012
0.025 –0.00625	0.033	0.034	0.032	0.032	0.026
0.0125–0.00625	0.017	0.016	0.016	0.016	0.013

TABLE XV

0°

N_1-N_2	100 water Volts	75 water 25 ethyl Volts	50 water 50 ethyl Volts	25 water 75 ethyl Volts	100 ethyl Volts.
0.1 –0.05	0.016	0.014	0.015	0.011	0.010
0.1 –0.025	0.033	0.030	0.031	0.028	0.022
0.1 –0.0125	0.049	0.046	0.042	0.041	0.035
0.1 –0.00625	0.064	0.058	0.059	0.049	0.049
0.05 –0.025	0.015	0.014	0.015	0.015	0.014
0.05 –0.0125	0.033	0.031	0.031	0.028	0.030
0.05 –0.00625	0.049	0.044	0.045	0.044	0.041
0.025 –0.0125	0.016	0.016	0.015	0.014	0.014
0.025 –0.00625	0.033	0.033	0.030	0.028	0.027
0.0125–0.00625	0.016	0.016	0.016	0.014	0.012

Table XVI

Concentration cells in water and ethyl alcohol. (Calculated)

25°

N_1-N_2	100 water Volts	75 water 25 ethyl Volts	50 water 50 ethyl Volts	25 water 75 ethyl Volts	100 ethyl Volts
0.1 -0.05	0.018	0.016	0.016	0.015	0.012
0.1 -0.025	0.033	0.032	0.032	0.030	0.025
0.1 -0.0125	0.049	0.050	0.049	0.045	0.042
0.1 -0.00625	0.066	0.067	0.065	0.061	0.058
0.05 -0.025	0.016	0.016	0.016	0.014	0.912
0.05 -0.0125	0.033	0.033	0.032	0.030	0.026
0.05 -0.00625	0.050	0.050	0.049	0.046	0.040
0.025 -0.0125	0.016	0.016	0.016	0.015	0.013
0.025 -0.00625	0.033	0.034	0.032	0.031	0.027
0.0125-0.00625	0.017	0.017	0.016	0.016	0.013

Table XVII

0°

N_1-N_2	100 water Volts	75 water 25 ethyl Volts	50 water 50 ethyl Volts	25 water 75 ethyl Volts	100 ethyl Volts
0.1 -0.05	0.016	0.015	0.016	0.014	0.011
0.1 -0.025	0.032	0.031	0.033	0.029	0.024
0.1 -0.0125	0.049	0.047	0.048	0.043	0.037
0.1 -0.00625	0.065	0.064	0.064	0.059	0.051
0.05 -0.025	0.015	0.015	0.016	0.016	0.012
0.05 -0.0125	0.033	0.031	0.032	0.028	0.026
0.05 -0.00625	0.049	0.048	0.048	0.045	0.040
0.025 -0.0125	0.017	0.016	0.015	0.013	0.014
0.025 -0.00625	0.034	0.032	0.031	0.029	0.028
0.0125-0.00625	0.016	0.016	0.016	0.016	0.014

Table XVIII

Molecular conductivity of silver nitrate in water and ethyl alcohol[1]

25°

N	100 water	75 water 25 ethyl	50 water 50 ethyl	25 water 75 ethyl	100 ethyl
0.10	99.46	54.60*	35.25*	24.75*	13.21
0.05	105.72	56.50*	37.92	27.02	14.34
0.025	110.22	59.79	39.58	30.52	17.05
0.0125	115.81	62.78	42.51	33.72	20.23
0.00625	119.86	63.85	45.20	36.03	23.95

---

[1] These conductivity values are taken from the work of Jones and Bassett, (Am. Chem. Jour., 32, 409 (1904)). Those marked * were obtained by interpolation.

TABLE XIX

0°

N	100 water	75 water 25 ethyl	50 water 50 ethyl	25 water 75 ethyl	100 ethyl
0.10	55.72	22.25*	14.75*	11.75*	7.84
0.05	58.63	23.75*	15.26	13.17	9.65
0.025	62.10	25.97	15.82	14.37	12.14
0.0125	63.16	26.76	17.09	16.88	13.76
0.00625	65.38	27.65	17.98	17.48	15.63

The results obtained for solutions of silver nitrate in water and methyl alcohol and in their binary mixtures are given in Table XX to XXVIII.

TABLE XX

Electrode potentials of silver in water and methyl alcohol

25°

N	100 water Volts	75 water 25 methyl Volts	50 water 50 methyl Volts	25 water 75 methyl Volts	100 methyl Volts
0.10	1.0105	1.0248	1.0412	1.0627	1.0958
0.05	0.9975	1.0128	1.0280	1.0520	1.0838
0.025	0.9831	0.9953	1.0139	1.0371	1.0713
0.0125	0.9702	0.9791	1.0020	1.0254	1.0631
0.00625	0.9555	0.9647	0.9900	1.0142	1.0496

TABLE XXI

0°

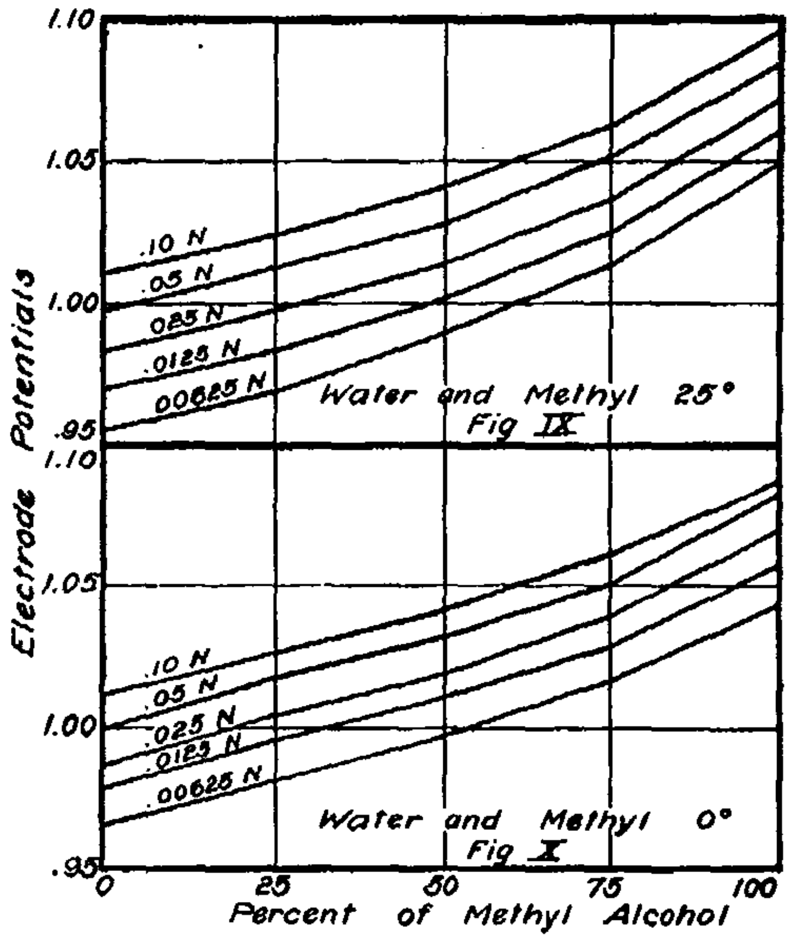
N	100 water Volts	75 water 25 methyl Volts	50 water 50 methyl Volts	25 water 75 methyl Volts	100 methyl Volts
0.10	1.0108	1.0263	1.0408	1.0608	1.0866
0.05	0.9995	1.0174	1.0314	1.0501	1.0814
0.025	0.9869	1.0034	1.0187	1.0390	1.0690
0.0125	0.9782	0.9953	1.0101	1.0284	1.0563
0.00625	0.9650	0.9834	0.9970	1.0170	1.0428

TABLE XXII

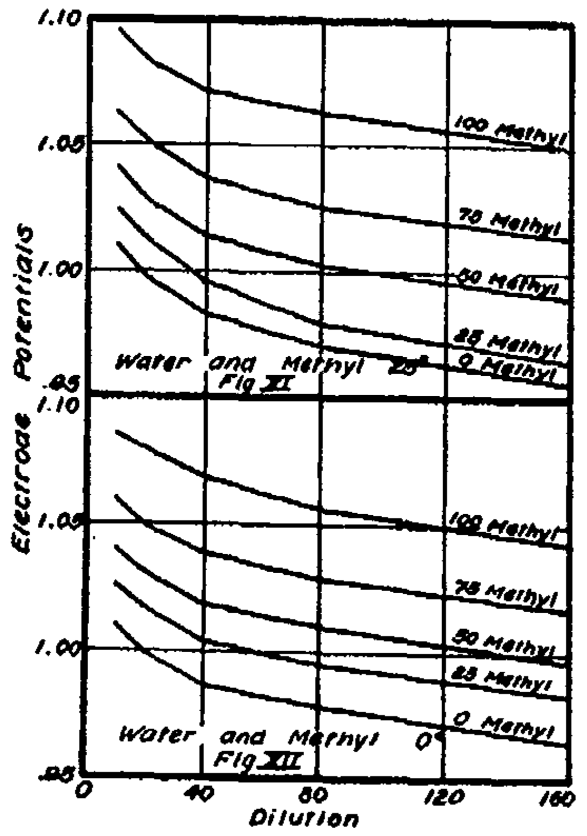
Temperature coefficients of electrode potentials of silver in water and methyl alcohol

N	100 water	75 water 25 methyl	50 water 50 methyl	25 water 75 methyl	100 methyl
0.10	—0.000047	—0.000058	—0.000015	+0.000071	+0.000332
0.05	—0.000080	—0.000183	—0.000132	+0.000072	+0.000111
0.025	—0.000154	—0.000323	—0.000188	—0.000074	+0.000086
0.0125	—0.000327	—0.000652	—0.000282	—0.000111	+0.000256
0.00625	—0.000394	—0.000760	—0.000371	—0.000112	+0.000268

The effect of change of solvent on the electrode potential is shown in Figs. IX and X. While these curves are straighter than those obtained for water and ethyl alcohol and their mixtures, they still show the more rapid drop on the methyl alcohol side of the curve. The effect of concentration on the electrode potentials in the water and methyl alcohol solutions



(Figs. XI and XII) is the same as has been found for the other solvents studied. The electrode potential of silver in pure methyl alcohol solutions stands between those for silver in aqueous and methyl alcohol solutions. This relation also holds for the relative positions of the solution tension of silver in the pure solvents. On the other hand, the values for the molecular conductivity of silver nitrate in methyl alcohol lie between those in water and ethyl alcohol.



As was observed above, the temperature coefficients in water solutions are negative while those in methyl alcohol are positive. Here again, the influence of the water manifests itself in the more dilute solutions of those binary mixtures which contain a high percent of methyl alcohol and this to a much greater extent than in the water-ethyl alcohol mixtures.

The observed electromotive forces of the concentration cells in water and methyl alcohol are recorded in Tables XXIII and XXIV, the calculated values in Tables XXV and XXVI. Here again the agreement is as close as could be desired.

TABLE XXIII
Concentration cells in water and methyl alcohol

25°

N_1-N_2	100 water Volts	75 water 25 methyl Volts	50 water 50 methyl Volts	25 water 75 methyl Volts	100 methyl Volts
0.1 -0.05	0.015	0.014	0.015	0.013	0.012
0.1 -0.025	0.033	0.031	0.030	0.029	0.020
0.1 -0.0125	0.045	0.047	0.048	0.047	0.039
0.1 -0.00625	0.062	0.061	0.051	0.056	0.056
0.05 -0.025	0.016	0.016	0.016	0.016	0.012
0.05 -0.0125	0.031	0.030	0.032	0.032	0.026
0.05 -0.00625	0.048	0.047	0.046	0.049	0.041
0.025 -0.0125	0.016	0.016	0.015	0.016	0.013
0.025 -0.00625	0.033	0.034	0.032	0.034	0.028
0.0125-0.00625	0.017	0.015	0.015	0.015	0.014

TABLE XXIV
0°

N_1-N_2	100 water Volts	75 water 25 methyl Volts	50 water 50 methyl Volts	25 water 75 methyl Volts	100 methyl Volts
0.1 -0.05	0.015	0.015	0.014	0.015	0.009
0.1 -0.025	0.033	0.029	0.030	0.030	0.025
0.1 -0.0125	0.048	0.047	0.044	0.040	0.036
0.1 -0.00625	0.064	0.061	0.058	0.055	0.049
0.05 -0.025	0.015	0.016	0.015	0.016	0.011
0.05 -0.0125	0.033	0.032	0.033	0.030	0.027
0.05 -0.00625	0.048	0.047	0.045	0.043	0.042
0.025 -0.0125	0.016	0.016	0.015	0.014	0.015
0.025 -0.00625	0.033	0.032	0.032	0.031	0.028
0.0125-0.00625	0.016	0.015	0.016	0.015	0.013

TABLE XXV

Concentration cells in water and methyl alcohol. (Calculated)

25°

N_1-N_2	100 water Volts	75 water 25 methyl Volts	50 water 50 methyl Volts	25 water 75 methyl Volts	100 methyl Volts
0.1 –0.05	0.018	0.016	0.015	0.014	0.012
0.1 –0.025	0.033	0.033	0.032	0.030	0.023
0.1 –0.0125	0.049	0.050	0.048	0.045	0.039
0.1 –0.00625	0.066	0.066	0.065	0.061	0.054
0.05 –0.025	0.016	0.016	0.016	0.015	0.011
0.05 –0.0125	0.033	0.033	0.033	0.031	0.027
0.05 –0.00625	0.050	0.050	0.049	0.047	0.042
0.025 –0.0125	0.016	0.016	0.016	0.015	0.013
0.025 –0.00625	0.033	0.033	0.033	0.031	0.028
0.0125–0.00625	0.017	0.016	0.016	0.016	0.015

TABLE XXVI

0°

N_1-N_2	100 water Volts	75 water 25 methyl Volts	50 water 50 methyl Volts	25 water 75 methyl Volts	100 methyl Volts
0.1 –0.05	0.016	0.015	0.015	0.015	0.012
0.1 –0.025	0.032	0.031	0.032	0.030	0.025
0.1 –0.0125	0.049	0.047	0.048	0.046	0.038
0.1 –0.00625	0.066	0.064	0.064	0.061	0.053
0.05 –0.025	0.016	0.015	0.016	0.015	0.011
0.05 –0.0125	0.033	0.032	0.032	0.030	0.027
0.05 –0.00625	0.050	0.048	0.049	0.047	0.041
0.025 –0.0125	0.017	0.016	0.016	0.016	0.014
0.025 –0.00625	0.034	0.033	0.032	0.031	0.028
0.0125–0.00625	0.017	0.016	0.016	0.016	0.014

TABLE XXVII

Molecular conductivities of silver nitrate in water and methyl alcohol[1]

25°

N	100 water	75 water 25 methyl	50 water 50 methyl	25 water 75 methyl	100 methyl
0.10	99.46	65.50*	49.25*	41.50*	35.77
0.05	105.72	68.75*	53.33	48.20	44.67
0.025	110.22	72.68	56.80	52.33	53.42
0.0125	115.81	75.56	59.75	57.17	62.95
0.00625	119.86	79.34	63.22	61.31	70.30

TABLE XXVIII

0°

N	100 water	75 water 25 methyl	50 water 50 methyl	25 water 75 methyl	100 methyl
0.10	55.72	30.50*	25.25*	25.60*	25.98
0.05	58.63	33.00*	27.27	27.98	32.63
0.025	63.10	35.63	28.63	30.03	39.71
0.0125	63.16	36.95	29.93	32.81	45.28
0.00625	65.38	39.03	31.47	35.22	50.09

The solution tension of silver in water, ethyl alcohol and methyl alcohol were calculated by means of the equation

$$\log P = \frac{\pi}{0.058} + \log\left(22.4 \cdot c \cdot \frac{\lambda_v}{\lambda_\infty} \cdot \frac{T}{273}\right)$$

For λ_∞ at 25° the following values were assumed: water = 128.54,[2] ethyl alcohol = 35.6,[2] methyl alcohol = 98.0.[3] The corresponding values for silver nitrate in the mixed solvents have not been determined.

The values of the solution tension of silver as calculated on the basis of each of the five concentrations in the three solvents are given for comparison.

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[1] Taken from the work of Jones and Bassett (Am. Chem. Jour., 32, 409 (1904)). Those marked * were obtained by interpolation.

[2] Kohlrausch: Sitzungsber. Berl. Akad., 26, 570 (1902).

[3] Völlmer: Loc. cit.

TABLE XXIX
Solution tensions of silver

N	Water	Ethyl alcohol	Methyl alcohol
0.10	2.49×10^{-17}	5.30×10^{-18}	1.54×10^{-19}
0.05	3.18	5.92	1.91
0.025	3.58	6.22	1.81
0.0125	4.50	6.67	2.15
0.00625	5.79	5.59	2.50
Mean,	3.91×10^{-17}	5.94×10^{-18}	1.98×10^{-19}

The solution tension of silver in the 0.10 *N* aqueous solution is almost identical with the value of 2.3×10^{-17} found by Neumann.[1] The mean value, which is slightly higher, is also in good agreement. The ratio between the solution tension of silver in water and in ethyl alcohol as indicated by the mean value is not so large as that found by Jones,[2] but is of the order 1 : 7 instead of 1 : 40. It will be observed also that there is unmistakable evidence of an increase in solution tension with increase in dilution for all three solvents.

The heats of ionization of silver calculated for the pure solvents and the fifty percent mixtures are given in Table XXX. Since it is impossible to obtain solutions containing one gram-equivalent weight of silver ions in all the solvents, the heats of ionization are calculated on the basis of the electrode potentials at the dilutions used. This gives us at least a basis for comparison. In the following table each value is the mean of ten different values, i. e., the mean of the values obtained for the five different concentrations in each solvent at the two temperatures:

TABLE XXX
Heats of ionization

Ethyl Cals.	Methyl	Water	50 water 50 ethyl	50 water 50 methyl	50 ethyl 50 methyl
+22727	+23126	+24063	+24293	+24541	+22973

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[1] Zeit. phys. Chem., 14, 193 (1894).
[2] Loc. cit.

The heat of ionization thus determined for silver in water is somewhat lower than that obtained by Ostwald[1] (26200 cals). It will be observed that the values for the water-alcohol mixtures are slightly higher than for the component solvents, while the heat of ionization in the fifty percent alcoholic mixture is very nearly the mean of the values in the two alcohols.

We shall extend this work as rapidly as possible to other pure solvents and their binary mixtures.

Summary

The electrode potentials of silver in solutions of silver nitrate in water, ethyl acohol, methyl alcohol and in binary mixtures of these solvents have been determined at 0° and 25°.

The electrode potentials are greatest in methyl alcohol and least in aqueous solutions, those in ethyl alcohol occupying an intermediate position.

The values of the electrode potentials are highest in the most concentrated solutions. They decrease rapidly with dilution at first and then afterward the decrease proceeds almost linearly with further dilution.

The electrode potentials in the binary mixtures of the two alcohols obey the law of mixtures. In the binary mixtures of water and the two alcohols, the electrode potentials increase slowly at first with addition of alcohol from the value in pure water up to mixtures containing about seventy-five percent of the alcohol and then more rapidly with further increase in the proportion of alcohol.

The temperature coefficients have been calculated for each concentration in each solvent used. In both of the alcohols and in their binary mixtures the temperature coefficients are positive. Those in ethyl alcohol, seventy-five percent ethyl and fifty percent ethyl alcohol increase with dilution, while the temperature coefficients in methyl alcohol and its seventy-five percent mixture pass through a minimum value.

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[1] Zeit. phys. Chem., 35, 337 (1900).

The temperature coefficients in the water and seventy-five percent aqueous solutions are negative and the value of these negative coefficients increases with dilution. The influence of the water as manifested by the temperature coefficients is displaced toward higher dilutions as the proportion of the alcohol in the mixture is increased.

The electromotive forces of all the possible concentration cells in all the above solvents have been determined and compared with those calculated from the electrical conductivities by means of the Nernst equation. From the agreement between the observed and calculated electromotive forces it can be seen that the Nernst equation can be applied not only to solutions in non-aqueous solvents, but also to solutions in binary mixtures of these solvents.

The solution tension of silver in each of the three solvents has been calculated. Its value in ethyl alcohol lies between that in water and in methyl alcohol.

The heats of ionization were calculated for the pure solvents and the fifty percent mixtures. The heat of ionization in methyl alcohol stands between those in water and ethyl alcohol. The values for the water-alcohol mixtures are slightly higher than those of the component solvents, while the heat of ionization in the fifty percent alcoholic mixture is very nearly the mean of the values in the two alcohols.

Physical Chemical Laboratory
The State University of Iowa

A CHEMICALLY RESISTANT GLASS LACQUER

BY PAUL J. FOX[1]

In the carrying out of exact solubility determinations where the substances investigated are only very slightly soluble, as well as in many physico-chemical investigations, and in analysis, the solubility of glass becomes a very disturbing factor. For example, some bottles of common glass of 240 cc capacity, being filled with distilled water and placed on the water-bath, yielded each enough soluble alkaline material to the distilled water to require about 4.0 cc tenth-normal acid for neutralization. Though there are kinds of glass now manufactured which are very insoluble to distilled water and some mild reagents, they are not so in alkalies of even moderate strength. Besides, glass vessels are often needed in shapes and sizes not to be had in the insoluble varieties of glass.

It seemed to the author worth while to experiment a little to see whether a chemically resistant lacquer might not be prepared which would adhere well to glass. For this purpose it is obvious that such substances as shellac, mastic, copal, etc., are not suited, as they are more or less soluble in alkalies. The only substances that appeared to meet the requirements were paraffin, ceresin, rubber, gutta percha, balata and chicle, the last two being related[2] to gutta percha. Of these, gutta percha and balata are useless, as, like pyroxylin, they peel off glass with extreme readiness—a property which, however valuable in other directions, makes them useless as a base for a glass lacquer. Pure rubber is somewhat better in this respect, but cannot be used alone. Chicle is extremely adherent to glass—a property which might make it valuable for some electrical purposes—but the sample used

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[1] Scientist in Soil Investigations, Bureau of Soils, U. S. Dept., Agriculture, Washington, D. C.

[2] A. Tschirch: Die Harze und die Harzbehälter, Vol. I, p. 889ff. Leipzig, 1906. A complete discussion of these bodies will be found here.

by the writer was somewhat attacked by alkali. As between ceresin and hard paraffin, there appears not much difference, but the ceresin seems to give a slightly smoother surface.

Of solvents, carbon disulphide is the most satisfactory, as it is the quickest to work with and generally gives the smoothest coat, at least without practice. However, if it is desired to avoid carbon disulphide on account of its poisonous and inflammable qualities, carbon tetrachloride or chloroform may be used, in which case the lacquer must be applied hot, as ceresin is not sufficiently soluble in cold carbon tetrachloride or chloroform.

The manner of preparing and using is as follows: Pour about 100 cc carbon disulphide over 15 grams pure unvulcanized rubber (procure a rather firm rubber). Let stand a few hours, or until the mixture becomes homogeneous. Add 30 grams white ceresin; cut in small pieces and add about 100 cc more of carbon disulphide. The consistency will vary according to the particular sample of rubber, but the addition of the ceresin makes the rubber "solution" less viscid, in which fact the advantage of the lacquer lies. It should be thinner than glycerin. The vessel to be treated is cleaned, rinsed with absolute alcohol and drained. It is then one-third filled with the lacquer, shaken gently around, and immediately drained. With a little practice it is easy to make smooth, translucent coatings. It is well to make the lacquer thinner and apply two coats, allowing a drying interval of 4–5 hours. If carbon tetrachloride is used, make the lacquer thicker and apply hot. As good coatings can be obtained with carbon tetrachloride as with carbon disulphide with a very little practice.

The coats will not endure long and violent shaking, but stand moderate usage very well. If injured, they do not peel away as a pure rubber or gutta percha coating does, but can be "repaired" at the point of injury.

Two common glass bottles of capacity 240 cc were treated as above described, and filled with distilled water of conductivity 2.45 reciprocal megohms (reduced to 20°). They were then placed in a thermostat and rotated for 70 hours, when they showed a conductivity (average) of 2.98 reciprocal megohms (reduced to 20°). Three blank bottles of same make and lot showed a conductivity (average) of 58.0 reciprocal megohms. In another test with similar bottles, a lacquered bottle was protected from the action of hydrofluoric acid sufficiently concentrated to dissolve 1.345 grams of material from a like but unprotected bottle, in the same time.

FLAME REACTIONS. III

BY WILDER D. BANCROFT AND HARRY B. WEISER

Electrolytic Flames

It has been shown previously[1] that all reactions tend to emit light and that all reactions do emit light providing the reaction velocity is sufficiently high. It ought to be possible, therefore, to bring about certain reactions electrolytically under such conditions that the electrolytic reactions would be accompanied by a luminescence. An effect of this nature was observed by Schluederberg.[2]

"Very dilute sulphuric acid was electrolyzed in a dark room with lead wire electrodes and an alternating current—3, 2, and 1 amperes. The solution fills up with a fine white precipitate of 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 give 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 a 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."

Wilkinson[3] followed up the observation of Schluederberg and used the direct current with several metals other than

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[1] Bancroft: Jour. Franklin Inst., 175, 129 (1913).

[2] Schluederberg: Jour. Phys. Chem., 12, 623 (1908).

[3] Wilkinson: Jour. Phys. Chem., 13, 691 (1909).

had. He obtained flashes of light of varying intensity in a number of cases.

This work was taken up with the end in view of studying in detail the reactions which produce the luminescence and of finding out what reactions and what conditions are necessary for securing a bright, continuous, electrolytic flame.

Electrolytic Flames with a Mercury Anode

The most striking of the electrolytic flames were those emitted during the electrolysis of alkali halide solutions using a mercury anode.

Before discussing the luminescence brought about by bringing mercury and the halogens in contact with one another electrolytically it will be interesting to note the color obtained by burning mercury in the halogens. The following method was found to work admirably even as a lecture experiment: A piece of glass tubing, fourteen inches long and one to one and one-fourth inches in diameter was supported horizontally. One end was supplied with a stopper containing an outlet tube leading to a suction pump in the hood; the other end was fitted with a tight stopper and a tube for conducting in the halogen vapors. This tube was drawn out to a jet at one end and the other end was attached to a chlorine cylinder; if used for bromine or iodine, the tube was bent at right angles and a small Erlenmeyer flask fastened to it. To carry out the experiment, a porcelain boat about three inches long was filled with mercury and placed in the large horizontal tube, so that it was just beyond the jet of the inlet tube for the halogen. The whole tube was then warmed slowly and carefully at first to minimize the danger of cracking. Finally, the heat was concentrated on the boat until the mercury began to vaporize. The halogen was then driven through the jet and the mercury took fire, burning brilliantly the full length of the boat. The flame burns sufficiently brightly so that in a darkened room one can see it distinctly at a distance of several yards. The color of the flame was as follows:

TABLE I

Metal	Halogen	Color of flame
Mercury	Bromine	Yellow to bright orange
Mercury	Iodine	Reddish orange as viewed through the iodine vapors
Mercury	Chlorine	Greenish yellow

We will now direct our attention to the mercury flames produced electrolytically. The apparatus used was as follows: A layer of mercury was placed in a flat crystallizing or petrie dish of a size varying from an inch to ten inches in diameter, depending on the amount of luminescent surface desired. A dish containing the mercury anode was then set in another crystallizing dish of slightly larger diameter. The solution was poured into the outer dish until it came up above the level of the inner dish. The layer of mercury was connected with the circuit by means of a wire insulated by sealing it into a piece of small glass tubing. For the cathode, a sheet of platinum about the size of the anode surface was used whenever practicable. For a lecture experiment where a very large anode surface is more effective, a cathode of copper wire gauze may be used instead of platinum. For ordinary work, storage cells giving from two to thirty-two volts were used as a source of current. With a large anode surface it was easier to get the necessary current by using the 110 volt D. C. with suitable resistance. As electrolytes 20 percent solutions of potassium bromide, potassium iodide, sodium chloride, and sodium sulphate, were employed. The brightest light was obtained by electrolysis of the bromide. This will be taken up in detail as a typical case.

On passing the current through the bromide solution, the mercury anode was quickly covered with a film of mercurous bromide and the whole surface glowed perfectly uniformly and very brightly. If the temperature of the electrolyte was about 18° or lower, the glow was bright enough to be seen in daylight and was conspicuously brilliant when viewed in the dark. The luminescence will last for a long time but the brilliancy gradually dies away, due to impoverishment and to the fact that the film becomes so thick that it cuts down the current and also masks the light. After the electrolysis has run for several minutes and the luminescence has become faint, it makes a striking experiment to open the switch, allow a little time for diffusion to take place and then quickly close the switch again. Under these conditions one gets an increase in the current passing through the solution and this is accompanied by a momentary bright flash that soon fades away as the current falls off. In the above experiment the brightest flame was obtained with a current density of about 1.5 amp/dm^2, the drop of potential being about 26 volts. A brighter luminescence was obtained when the electrolyte was at 0° than when at room temperature.

In striking similarity with the results obtained by direct chemical combination the color of the luminescence was found to be as follows:

TABLE II

Metal	Anion	Color of luminescence
Mercury	Br	Very bright orange
Mercury	Cl	Yellow to orange yellow
Mercury	I	Orange—not so bright as with Br
Mercury	SO_4	Yellow (greenish)

The question that naturally arises at this point is, what reaction produces the light? From the experiments on direct union we might infer that the luminescence is produced by the corrosion of massive mercury by the nascent halogen altogether independent of any other factors. That this first apparently obvious inference is inadequate to explain the phenomenon is seen from the fact that there is no visible luminescence until a film is formed. During the electrolysis the corrosion of the mercury by the nascent halogen is plainly going on and if our first assumption is correct this should give light regardless of the presence or absence of a film. That no luminescence is produced until the film is formed may be seen very clearly by observing the electrolysis of potassium iodide with a mercury anode at different current densities and temperatures. In this case the mercurous iodide formed is fairly soluble in the electrolyte and the iodide will dissolve until saturation is reached in the immediate region of the anode, after which the film will form. The time of formation of the film and hence of the flame depends on the current density and the temperature. In this experiment an anode of about one-quarter centimeter surface was used and accurate measurements were made of the initial current and voltage and of the current and voltage just after the formation of the film. The time necessary for the formation of the film and the appearance of the light was noted, and also the temperature. In the following table C_i, C_f, V_i, V_f denote the initial and final currents and the initial and final voltage, respectively.

TABLE III

C_i	C_f amps	V_i volts	V_f volts	Light seconds	Temp.
0.160	0.075	3.5	14	4	— 2°
0.060	0.040	2.4	10	40	— 2°
0.060	0.040	2.0	11	180	60°
0.060	0.042	1.5	9	275	98°
0.160	0.030	2.5	6	15	18°
0.060	0.010	2.0	4	128	18°

Table III shows the importance of the film in producing electroluminescence. The same effect observed in the electrolysis of potassium iodide may be noted in other cases to a very much less marked degree. For example, in the electrolysis of potassium bromide with a mercury anode at high temperatures there is a very short interval between the closing of the switch and the appearance of the film and the flame.

Since it has been found in all cases studied that the presence of a film over the anode is necessary for the formation of the anode flame observed, the question comes up.

as to the function of the film. Since the formation of the film is accompanied by an increase in voltage, the first assumption is that the luminescence is produced by an effect similar to a silent discharge or sparking through the film. A number of experiments have been carried out which show that this is not the case.

Marked evidence against the glow being a sparking effect is to be seen in the perfect uniformity of the luminescence over the whole surface of the anode altogether irrespective of the size. This would probably not be the case if it were a discharge through the film, for the film would unquestionably break down at some place and produce a distinct spark. No such effect was noted. Furthermore, the film may be scratched or broken at some point and then the circuit closed. Under these conditions, if the glow were a sparking effect, we should certainly expect the energy of the current to spark across this little gap rather than through the difficultly conducting film. Although this experiment was tried a number of times no flash of the nature of a spark was ever observed.

The luminescence is not through the film but *underneath* it, in direct contact with the mercury surface. This may be told from the fact that, after a little time, the film becomes sufficiently thick that it looks black and the glow is masked as the light from an incandescent bulb would be if surrounded by a piece of thin black cloth. After the film is so thick that but very little light can be seen on looking down upon it, a thin region of luminescence may be observed between the mercury and the film by looking sidewise parallel to the mercury surface. This indicates that the glow is not in the film but only at the mercury surface. A further test of this was made in the following manner: Electrolysis of the bromide solution with a mercury anode was carried out for a few minutes. The anode dish was carefully removed from the solution without cracking the film. The latter was then washed by allowing a gentle stream of water to flow over it for a long time. After washing, the excess of water was taken up with filter paper and the film allowed to dry thoroughly. A piece of platinum about one square centimeter in area was held against this film as firmly as possible without breaking it. This piece of platinum was made cathode and the mercury anode. On closing the circuit there was no arcing through the film even though the voltage was increased to 40 volts. The film at the edge of the platinum cathode was then moistened with a very small drop of dilute potassium bromide solution. On closing the circuit a distinct glowing was seen not through but *underneath* the portion of the film that was dampened.

A further proof that the anode flame is not caused by a sparking through the film was obtained by electrolyzing two solutions of potassium bromide in series—one hot and the other cold—with a mercury anode. Under these conditions it was found that the flame was much brighter and lasted much longer in the cold than in the hot solution. However, the voltage drop across the hot solution *was greater* than across the cold solution. This is diametrically opposite to what we should expect if it were a case of sparking through the film. The following table shows this point clearly. The temperature of the hot solution was 54° and of the cold solution, —4°.

TABLE IV

Time seconds	Voltage cold	Voltage hot	Time seconds	Voltage cold	Voltage hot
5	12.00	9.00	55	9.42	12.37
10	10.20	10.90	60	9.39	12.42
15	9.98	11.50	75	9.33	12.46
20	9.80	11.81	90	9.30	12.50
25	9.65	12.00	105	9.25	12.55
30	9.60	12.10	120	9.24	12.57
35	9.55	12.15	150	9.23	12.60
40	9.50	12.23	180	9.22	12.60
45	9.48	12.26	240	9.20	12.62
50	9.47	12.28			

If the electroluminescence were produced by a silent discharge through a thin film of a mercury halide, glowing should result, if such a violent discharge were passed through a thin film artificially prepared. An experiment to test this was carried out.

Two test tubes were taken, one about three-fourths of an inch internal diameter and the other about one-half inch external diameter. The larger was coated on the inside and the smaller on the outside with a thin uniform film of mercuric chloride. To do this a saturated solution of mercuric chloride in ether was prepared and the surface to be coated was wetted uniformly with this. The ether evaporated quickly leaving a thin coating of the salt on the tube. This was repeated until a film of the desired thickness was secured. The larger test tube, which was coated on the inside, was surrounded by another slightly larger and the intervening space filled with dilute sulphuric acid. The smaller test tube which was coated on the outside, was filled with dilute sulphuric acid and then placed inside the larger one and the two were held apart concentrically by a cork. We thus had an apparatus on the plan of the Siemens-Halske ozonizer. By connecting this with the terminals of an induction coil, a silent discharge was passed through the thin film and across the gap be ween the test tubes. When this was done in a dark room only a faint whitish glow was obtained, in no way resembling the orange or yellow luminescence obtained on electrolysis. The experiment was repeated a number of times with varying thickness of film but always with the same result.

It is evident from the above series of experiments that the luminescence is not due to a sparking through the film but is due to the reaction taking place in the region possibly of molecular dimensions, between the surface of massive mercury and the film of salts. With the possibility of a sparking effect through the film removed from consideration, we can again turn our attention to the conditions and to the consequent reaction which produces the luminescence.

Practically all of the resistance and therefore the heating effect of the current is produced by the film. Although the current and the voltage for obtaining the maximum luminescence are relatively low, the heat generated is confined to a very small space and, being in direct contact with the mercury surface, is sufficient to vaporize minute quantities of mercury, which in the presence of the nascent halogen, will react with sufficient velocity to emit the observed luminescence. Considerable evidence points to the fact that the luminescence of the mercury anode is due to the rapid union of the anion with heated metal vapor to form the solid salt.

It was found necessary in the experiments on direct union, discussed at the beginning of this paper, to heat the mercury until it began to vaporize before the reaction velocity was sufficiently high to produce luminescence. Some experiments were tried with mercury in the cold. A drop of bromine was allowed to fall on a massive mercury surface in a dark room. The reaction took place rapidly with the evolution of much heat, but the reaction velocity was not sufficiently high to cause glowing. A very fine stream of mercury was sprayed into dense fumes of bromine. Here again the reaction took place rapidly, but the velocity was not high enough to produce light. If, however, the mercury were heated, the velocity of the reaction was such that a very bright light was produced. We have exactly this same thing in the electrolytic process. No light is emitted until the film is formed and then heat generated in direct contact with the anode surface volatilizes small amounts of mercury, which react rapidly with the nascent anion to form the solid salt.

A further argument in support of this view is that by far the brightest luminescence on electrolysis is obtained with mercury—a metal with a relatively low vaporization point—while with a metal like copper or silver only a very faint glow can be obtained even under the most favorable circumstances.

One other point must be considered. Reference has repeatedly been made to the fact that the anode flame is brighter and lasts longer in the cold solution than it does in the hot. This is particularly noticeable in the electrolysis of the bromide solutions and is much less marked in the case of the chloride and iodide. So marked is it in the bromide electrolysis that attention was called to the fact that for demonstration purposes the cold solution should always be used on account of its greater effectiveness. One explanation of this effect of temperature on the luminescence is, that other conditions being the same, chemiluminescence may increase with decreasing temperature. There is some evidence[1] in support of this view but the temperature difference is so small in the bromide electrolysis compared with the difference in the luminescence observed, that this explanation seems doubtful.

If we are not to assign a very large negative temperature effect to the luminescence of the mercury-bromine reaction, we must find some other explanation for the marked change in luminescence due to cooling the solution a few degrees. If we consider—as we apparently have to—that the formation of the solid salt is essential to the luminescence in this particular case, the effect of the temperature of the solution may be due to the change in solubility and degree of supersaturation with change of temperature. Although the absolute solubility of mercurous bromide is very small both at 0° and at 50°, the relative solubility is undoubtedly greater at the higher temperature than at the lower. From what we know of other solutions it is certain that the absolute amount of supersaturation increases with rising temperature. At the lower temperatures we shall therefore have the mercurous bromide not only precipitating as fast as formed but practically at the point where formed. The space within which the mercurous bromide precipitates is therefore very small. At higher temperatures the solubility and supersaturation increase, and consequently the mercurous bromide will have a chance to diffuse to a certain unknown extent before precipitation completely and the space throughout which the precipitation takes place is relatively much larger. This involves introducing the further conception that the intensity of lumines-

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[1] Dewar: Chem. News, 70, 252 (1894); Bancroft and Weiser: Trans. Am. Electrochem. Soc., 25, 127 (1914).

cence increases with increasing volume concentration as well as with increasing reaction velocity.

The luminescence of the mercury-bromine reaction becomes in part a crystalloluminescence, like the whitish light obtained when sodium chloride crystallizes under suitable conditions, when sodium burns slowly in chlorine, or when cathode rays act on crystals of sodium chloride. This follows from the facts: that we get no luminescence until the mercurous bromide precipitates; that the luminescence does not necessarily vary directly with the fall of potential at the anode; and that the luminescence varies more with the temperature of the solution than can reasonably be accounted for solely on the assumption of a negative temperature coefficient.

From a study of the electrolytic mercury flames we come to the following conclusions:

1. A film must form over the anode before luminescence is obtained.

2. The luminescence is not produced by the thermoluminescence of the highly heated film or by a sparking through the film.

3. The effect of the film is to cause a rise of temperature in a very limited region in direct contact with the mercury sufficient to vaporize small quantities of the metal.

4. Luminescence is produced by the rapid reaction of nascent halogen with the heated mercury and the formation of the solid mercury salt.

The electroluminescence obtained with a mercury anode was by far the most spectacular and was obtained with the least difficulty. The current density was always comparatively low and a continuous glowing for several minutes was not hard to obtain. With the other metals studied the current density had to be considerably higher. As noted in the experiments on the mercury flames, no luminescence was obtained unless a film was formed. Furthermore, the film formed had to be of a firm, coherent nature and poorly conducting, so that a local heating in the region of the metal would result. The presence of such a film was found to be necessary in all cases for the production of electroluminescence. The presence of this film often masked the light emitted under it, so that a flash was all that was ordinarily obtained, after which the film was too thick to allow the faint glow to be seen through it. It occurred to us that if some means were employed to remove the most of the film as fast as formed, a continuous electroluminescence ought to be obtained. This was found actually to be the case. The method was simply to rotate the electrode rapidly and hold a brush against it which scraped away the excess film that masked the light. The apparatus used was simple in construction: A rotating electrode holder was held firmly in place on a stationary stand. The holder was supplied with a series of pullies so that different rates of rotation could be obtained. A 1/8 H. P. alternating current motor drove the belt. The anodes used were rods of the metal from one-half to 1 centimeter in diameter. The electrolyte was placed in a crystallizing dish four inches in diameter and four inches deep. This was only half filled so as to prevent the splashing of the electrolyte by the rapidly rotating anode. A stiff-bristled tooth brush served for brushing the electrode. In the actual experimentation the electrode was first started, the brush held firmly against it and the current was then passed through the solution.

A detailed account will now be given of the separate experiments with anodes of tin, copper, cadmium, silver, and lead in 20 percent solutions of hydrochloric acid or sodium chloride, potassium bromide, potassium iodide, sodium sulphate, or sulphuric acid.

Electrolytic Flames with Tin Anode

Tin Anode in Sodium Chloride Solution.—In this electrolysis no coherent film was produced on the anode but instead a slimy deposit was formed around it. This deposit was due to the hydrolysis of the chloride formed and could be prevented by acidifying. There was no luminescence even at a very high current density. There was no sparking effect whatsoever until the solution became so hot that it boiled around the electrode.

Tin Anode in Potassium Bromide Solution.—No coherent precipitate was formed on the anode and hence no luminescence was obtained even at a very high current density and voltage. There was no sparking until the solution became boiling hot around the anode. On first closing the switch the electrode appeared dark, due to some bromine set free at the high current density. Immediately thereafter a dense white precipitate formed in the region of the anode, due to the hydrolysis of the bromide formed on the electrolysis.

Tin Anode in Potassium Iodide Solution.—On passing the current through this solution a film of insoluble iodide was immediately formed on the surface of the electrode. This film was firm and coherent and a luminescence was obtained as one would expect from analogy with the experiments using a mercury anode. By starting with a clean anode and a clear solution a faint light can be detected at 1 amp/cm^2 and 11 volts. In order to see this, however, one's eyes must have become very sensitive by remaining a long time in the dark. Even then only a flash was observed that was greenish white in color. The corrosion of the anode was not quantitative and the liberated iodine soon colored the solution. By increasing the current density to 1–1.5 amp/cm^2 and a voltage of 20, a much brighter luminescence was secured. If the anode was rotated rapidly and brushed, the glow was continuous and was greenish white to greenish yellow in color.

Tin Anode in Sulphuric Acid Solution.—At 0.1 amp/cm^2 and 6 volts a faint greenish white light was obtained. At a slightly increased current density and 10 volts, the luminescence was continuous and was greenish yellow in color. By increasing the current density and so increasing the reaction velocity still more, this greenish yellow flame was bright enough that it could be seen distinctly across the room. A very thin film formed over the anode. This may be verified by polishing the electrode until it is bright before starting the electrolysis. As soon as the switch was closed, the shiny surface became dulled by the formation of the thin film. Furthermore, the current gradually became less and less, indicative of the film becoming thicker.

It is interesting to compare the luminescence obtained on electrolysis with the flame secured by direct union of the metal with the halogen, Table V. The method of obtaining the results on direct union have been described in a former paper.[1]

TABLE V

Metal	Anion	Color of electroluminescence	Color on direct union
Tin	Cl	No light	Bluish violet to green
Tin	Br	No light	Green
Tin	I	Greenish white to yellow	Light green (yellowish)
Tin	SO_4	Greenish white to yellow	

Electrolytic Flames with Copper Anode

Copper Anode in Hydrochloric Acid.—In this electrolysis the light effect was faint, even at a high current density, but it was clearly seen to be greenish white in color. The luminescence appeared as a flash on first closing the switch but gradually grew fainter and fainter. By rotating the electrode rapidly this faint glow may be obtained continuously. A thin film of cuprous chloride was formed on the surface of the anode.

Copper Anode in Potassium Bromide Solution.—The light effect was very weak indeed, but if the eyes were allowed to become sensitive, a glow could be seen around the electrode at one to two amperes per square centimeter and twelve volts. The solution became colored by some bromine liberated at the high current density and by the formation of a reddish brown precipitate. On this account it was difficult to determine the exact color of the whitish luminescence. With a rotating electrode the glow lasted for some little time. No sparking was obtained until the solution boiled around the electrode and the voltage increased to 35 to 40 volts. The sparks were distinctly green flashes.

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[1] Bancroft and Weiser: Jour. Phys. Chem., 18, 313 (1914).

Copper Anode in Potassium Iodide Solution.—A very faint glow was obtained at 15 volts and a high current density, 1–2 amp/cm^2. This was observed only after staying for considerable time in the dark room before starting the electrolysis. The light was reddish white tinged slightly with green. No doubt the color was greenish white and the reddish appearance was due to looking through an intensely red solution. The red color of the solution was due to iodine set free at the high current density of the electrolysis. Examination of the anode after electrolysis showed that a film of cuprous iodide was formed on it. The luminescence could be observed for only a few seconds even with a rotating electrode on account of the dark color of the solution entirely masking the faint anode glow. That this was the case may be verified by observing the electrolysis in daylight. The electrode was placed near the edge of the container in a clear solution of the iodide. A moment after the switch was closed the electrode was obscured by the liberated iodine coloring the solution a dark red.

Copper Anode in Sulphuric Acid Solution.—At a relatively low current density and seven volts a flash of light was obtained but it lasted only a moment. It was greenish in color. By increasing the current density slightly and rotating the electrode, this glow became brighter and was of a greenish yellow color. A film, apparently of oxide, was formed on the surface of the electrode. At a high current density no light was obtained for no film was formed. Instead, the disintegration of the anode was so rapid that the surface seemed to be torn off and the solution filled up with fine particles of copper.

Summary.—In all of the above cases it was found that an electroluminescence was obtained, but the glow was only very faint and was difficult to get continuously. The quality of the luminescence was hard to recognize, owing to the faintness of the glow and the fact that the solution became cloudy after the electrolysis. For the most part the light was greenish white in color. From a knowledge of the conditions necessary for obtaining a bright electroluminescence we should expect to get only a faint light with a copper anode. The metal volatilizes at a very high temperature and the film formed is of a slimy amorphous character rather than of the firm, coherent nature which we found to be necessary for obtaining the mercury flames.

Electrolytic Flames with Cadmium Anode

Cadmium Anode in Chloride Solution.—During the electrolysis in sodium chloride solution a white amorphous precipitate formed in the region of the anode. On account of the nature of the precipitate there was of course no luminescence. In hydrochloric acid solution no precipitate whatsoever was formed. By increasing the current density so high that the solution boiled around the electrode, sparks were obtained. These sparks were of a greenish color.

Cadmium Anode in Potassium Bromide Solution.—What has been said regarding the chloride electrolysis applies to the bromide. No coherent film deposited on the electrode; instead an amorphous precipitate was formed. There was no luminescence.

Cadmium Anode in Potassium Iodide Solution.—A faint flash of light was obtained at 0.5 amp/cm^2 and ten volts. At a slightly increased current density and 20 volts a very bright yellow luminescence was obtained. The film of iodide formed on the anode was so resistant that it quickly cut down the current with a stationary anode. In order to obtain the luminescence continuously it was found necessary to rotate the electrode 3000 r. p. m. and to hold a stiff-bristled brush firmly against it. Under these conditions the film was removed sufficiently rapidly that the yellow luminescence lasted for a considerable time. When the observation was made at a relatively low current density or in the hot solution, results were obtained similar to those observed with a mercury anode in potassium iodide solution. The iodide of cadmium dissolved appreciably in potassium iodide, particularly in the hot solution, so that the film did not form as soon as the switch was closed. As in the case of the mercury flame in iodide solution, there was an interval of time between the closing of the switch and the appearance of the flash. The length of this time interval depended on the current density and the temperature.

Cadmium Anode in Sulphuric Acid Solution.—In this electrolysis the film did not appear immediately and so a similar phenomenon to that above mentioned was observed. Starting at a current density of about 1 amp/cm^2 and eight volts, the film formed in about two seconds. Simultaneously with the appearance of the film, the voltage increased to twenty-six volts and the current dropped off considerably. The luminescence was quite bright and was yellow in color with a tendency toward a greenish tinge. Even with a rotating electrode the glow would not last very long but gradually faded away. The thin film of oxide was so hard to remove that scraping with a fiber brush was insufficient to keep the electrode clean. By breaking the circuit and letting it stand for a moment in the acid solution the film dissolved off and the experiment could then be repeated.

Summary.—A cadmium anode in chloride and bromide solution gave no electroluminescence since no film was formed. In iodide and sulphate solution a film was formed and a bright electroluminescence of a yellow color was obtained. The color of these electrolytic flames was the same as that observed when volatilized cadmium was burned in an atmosphere of oxygen or chlorine.

Electrolytic Flames with a Silver Anode

Silver Anode in Hydrochloric Acid.—At a current density of 0.2 amp/cm^2 and 10 volts a flash was obtained that was rather faint and was yellowish white in color. By increasing the current density a brighter flash obtained but the film of chloride quickly shut off the light. This film was hard to remove and the voltage was high but there was no sparking.

The voltage was kept down by very vigorous brushing and the glow could be maintained for a few seconds.

Silver Anode in Potassium Bromide Solution.—A faint greenish yellow light was observed at a current density of 0.3 amp/cm^2 and 15 volts. The voltage rose gradually and the current fell unless the electrode was brushed very vigorously. Under these conditions the faint glow was maintained continuously.

Silver Anode in Potassium Iodide Solution.—A very faint orange glow was obtained at 11 volts. At a current density of 1 amp/cm^2 and 18 volts the orange luminescence was fairly bright and lasted for several seconds if the electrode was brushed.

Silver Anode in Sulphuric Acid Solution.—At 0.5 amp/cm^2 and 10 volts a faint glow was observed. The color was white with a slight yellowish tinge. At 1 amp/cm^2 with a rotating electrode a much brighter yellowish white luminescence was obtained.

Summary.—With a silver anode a coherent film was formed and luminescence was obtained in every electrolysis studied. The glow was never bright but could be obtained continuously by brushing the rotating cathode vigorously.

Electrolytic Flames with a Lead Anode

Lead Anode in Sodium Chloride Solution.—At 2 amp/cm^2 and 20 volts a faint glow was observed. The voltage rose rapidly and the current fell off even though the rotating anode was brushed hard. The luminescence was white.

Lead Anode in Potassium Bromide Solution.—Only a faint white light was obtained even at high current density. The film was not of a coherent nature and the solution filled up quickly with a dense precipitate which rendered the solution so cloudy that even with a rotating electrode the light effect could be seen for only a few seconds.

Lead Anode in Potassium Iodide Solution.—At 0.5 amp/cm^2 and 11 volts a bright yellow light with a greenish tinge was obtained. Even a moderate amount of brushing served to keep the anode sufficiently clean that a continuous luminescence was secured. At a slightly higher current density and a voltage of 20 volts the flame was visible at a distance of several yards. At the higher current density the electrode had to be brushed pretty vigorously to maintain the glow with undiminished intensity. The solution quickly became cloudy and the luminescence appeared much brighter by looking down on the electrode from above instead of through the turbid solution.

Lead Anode in Sulphuric Acid Solution.—At the beginning of this paper attention was called to the work of Schluederberg with lead electrodes in sulphuric acid, using an alternating current. He was unable to obtain a glow with the direct current on account of the formation of a film of lead peroxide. From analogy with the experiments above described we should expect to obtain a flash even with a direct current. As a matter of fact a fairly bright white glow was obtained for an instant. The attempt was made to remove the lead peroxide film by brushing and so obtain a continuous white luminescence with the direct current. It was found that the glow could be prolonged somewhat but the film stuck so tightly that it could not be removed sufficiently rapidly to obtain a continuous luminescence.

Summary.—A faint luminescence was obtained with a lead anode in chloride and bromide solution; in iodide solution the glow was relatively very bright and could be maintained for several minutes by rotating the electrode and brushing. A bright flash was obtained in sulphuric acid solution even with a direct current. A continuous glow may be secured using an alternating current thereby preventing the film of lead oxide becoming so thick that it cuts down the current until no luminescence is visible.

The results of this paper may be summarized as follows:

1. Reactions may be brought about electrolytically under such conditions that they emit light.

2. A particular study has been made of the luminescence and the conditions for obtaining luminescence in the elec-

trolysis of chloride, bromide, iodide, and sulphate solutions with a mercury anode. This study was extended using anodes of tin, copper, cadmium, silver, and lead.

3. In all cases in which luminescence was obtained, a firm, coherent film formed on the anode. In certain cases in which the product of the anodic reaction was soluble in the electrolyte, the film formation was delayed for a time. No luminescence appeared until after the film formed.

4. The luminescence was not due either to the thermoluminescence of the film or to a sparking through the film. It was underneath the film in the reaction zone.

5. A poorly conducting film is necessary. The heat generated by the resistance causes a local rise in temperature at the surface of the metal. The reaction which emits the light is the reaction of the nascent anion with the heated (and presumably volatilized) metal to form the solid salt.

6. No luminescence was obtained unless the metal in corroding formed the solid salt instead of dissolving or decomposing. Ordinarily the solubility is least and the stability is greatest in cold solution. In consequence of this we should expect the luminescence to be greater in the cold than in the hot solution. This was particularly noticeable in the electrolysis of potassium bromide with a mercury anode.

7. In many instances the heated metal will burn brightly in an atmosphere of oxygen or of the halogens. Under these conditions the color of the flame is strikingly similar to that obtained electrolytically.

8. With a stationary anode the luminescence is usually only a flash, since the film masks the luminescence and also cuts down the current so that the reaction velocity is very low.

9. In most cases the luminescence can be made continuous by rotating the anode rapidly and at the same time brushing it with a tooth-brush so that the film does not become too thick.

Cornell University

NEW BOOKS

La Silice et les Silicates. *By Henry Le Chatelier. 17 × 25 cm; pp. 574 Paris: A. Hermann et Fils, 1914. Price: 15 francs.*—The author points out, p. 1, that the text-books on chemistry usually say relatively little about silica and less about the silicates. He says, p. 7, that silica "is a regular proteus showing more numerous variations than any other known substance. The forms of crystallized anhydrous silica fall into two groups distinguished by a considerable difference of density: a mean density of 2.6 for the one and of 2.3 for the other. Carbon and phosphorus are the only other substances which show as large differences of density between the allotropic forms. Each of the groups contains two or three allotropic forms, distinct as regards their crystalline forms, and each of these forms undergoes reversible changes under the influence of heat, yielding a series of new forms stable only between certain temperature limits. There are certainly a dozen allotropic forms of silica....

"It is distinctly interesting to note the ease with which silica assumes the amorphous state and confers the same on the mixture which it forms with other silicates, thus giving rise to the ordinary glasses. No other substance in inorganic chemistry has this property to such an extent. It is true that boric acid occurs in the amorphous state; but its change to the crystallized is unknown and consequently it does not lend itself, as does silica, to a study of the change from the solid amorphous state to the crystallized state.

"Hydrated silica is not less interesting than crystallized anhydrous silica. It appears not to follow the laws of definite proportions and of constant dissociation pressures. Its water content varies indefinitely with varying external conditions. One of its striking properties is the formation of colloidal solutions with water. It is an open question whether these gelatinous masses are really hydrated in the chemical sense of the word or whether they are not rather due to very finely divided anhydrous silica forming a paste with water.

"The metallic silicates offer a field for study not less varied than that of silica itself. While other acids seem only to form a fairly limited number of salts, whose composition is governed by definite and very simple rules, the number of silicates seems almost to be unlimited and the formulas are sometimes so complicated that the law of simple proportions between the oxygen of the acid and that of the base becomes hard to confirm. An entire science, mineralogy, is devoted to the study of natural minerals and at least three-quarters of these are silicates. While it has been difficult to reproduce synthetically some of the natural silicates, there have been prepared in the laboratory a large number of silicates not found in nature. The study of these compounds will certainly give rise some day to a branch of chemistry comparable in importance with that of the carbon compounds."

The subject is treated under the general headings: chemical properties of the oxygen compounds of silicon; so-called hydrated silica; amorphous silica; crystallization of quartz; physical properties of quartz; rotary polarization; double refraction; chalcedony; silica having a low density; transformations of silica; general properties of glasses; chemical properties of glasses; physical properties of glasses; expansion of glasses; optical properties of glasses; metallic silicates; classification of metallic silicates; alkali and barium silicates; calcium silicates; magnesium silicates; aluminum silicates; ceramics; rocks and slags.

The author considers, p. 23, that the leucones are hydrates of silicon monoxide, $SiO.H_2O$ and $Si_3O_3.H_2O$, for instance. He bases this conclusion chiefly on the fact that caustic potash reacts with $SiO.H_2O$, causing the evolution of hydrogen. Another interesting conclusion, p. 76, is that a silicic acid jelly is merely a paste of anhydrous silica and water. "The presence in the silicic acid jellies of a substance as hard as anhydrous silica ought to be made evident if we use the paste to polish hard substances such as metals. The prediction has been confirmed experimentally. It proved easy to polish bronze by means of gelatinous silica, obtained by the decomposition of silicon fluoride by water. It was washed with distilled water and was not allowed to dry because this would have given rise to harder lumps through agglomeration." This is a very striking experiment but it seems open to the criticism that the anhydrous silica may have been formed during the polishing as a result of pressure.

The author inclines, p. 367, to the view of Tschermak that the feldspars form a continuous series between $6SiO_2Al_2O_3.Na_2O$ and $2SiO_2Al_2O_3.CaO$. On pp. 476 et ff the author discusses the theory of plasticity in considerable detail. He is strongly of the opinion that a *lamellar structure is essential*. *The reviewer* is not willing to go this length. It is clear that one can have more slipping with a lamellar than with a spherical structure; but it is putting the cart before the horse to make the lamellar structure the cause of plasticity. The essential for a plastic mass is that there shall be a film which shall be coherent and self-healing. In the case of putty the film is oil; in the case of wet sand it is water. If we are going to stipulate, as is usually done, that the plastic mass shall dry or bake to a solid mass, the film cannot be a liquid alone but must be a more or less gelatinous mass.

On p. 511 the author mentions a very interesting fact in regard to Etruscan pottery. This has to be burned at a temperature of 1000° and melts at 1070°. Consequently there must have been an extremely careful temperature regulation.

Under petrified wood, p. 206, the reviewer would have welcomed a discussion of the probable method of formation. Even if this had amounted chiefly to a confession of ignorance, it would have been worth while as calling attention to the gaps in our knowledge. A more extended discussion of colloidal silica would also have been a good thing, pp. 29, 65. One can get so much out of this book that one is tempted to ask for even more. *Wilder D. Bancroft*

Lehrbuch der Metallographie. *Chemie und Physik der Metalle und ihrer Legierungen. By Gustav Tammann. 17 × 25 cm; pp. iii + 390. Leipzig: Leopold Voss, 1914. Price: paper, 19 marks; bound, 20 marks.*—More work on alloys has been done in Tammann's laboratory than anywhere else, and consequently a text-book by him is welcome. The book aims to be a great deal more than a compilation of diagrams. For instance, 136 pages are given to one-component systems under the subheads: the process of crystallization; changes in properties with changes in state; changes in the properties of metals on working. Under two-component systems nearly fifty pages are devoted to the properties of binary alloys. The author does not agree with Beilby's views as to the formation of an amorphous phase when metals are polished or rolled, and for that we are truly grateful. It has always been a surprise to the reviewer that neither Beilby nor any of his supporters has ever made any attempt to confirm his hypothesis by experiments on transparent crystals of some sort.

While the plan of the book is excellent and while it is a valuable work, the avowed intention of the author to confine himself very largely to the work of his own laboratory makes the book more one-sided than was necessary or desirable. There is practically nothing on the corrosion of alloys, though that is quite as important as some of the other properties considered. Under electrolytic copper the work of Bennett has been overlooked. Too much stress has of course been laid on the method of thermal analysis, which is admittedly an easy and rapid method; but, unfortunately, also a crude one, especially when reactions between solids are involved.

The author adopts the view, p. 245, that Fe_3C is always an instable form and he does not even refer to Upton's suggestion of the possible existence of Fe_6C. The reviewer is quite certain that this is wrong. It is quite true that some graphite-free cast irons will set free graphite if anealed at 900°-1000°; but it does not follow from this that graphite is the stable phase at that temperature. That would be true only in case the graphite were not taken up again. Since it is possible to prepare alloys containing 3% carbon which do not set free graphite when annealed, it is clear that there has been an error due to not identifying the phases present before annealing.

In spite of these shortcomings, the book is by far the most interesting work on the subject with which the reviewer is familiar. It is to be hoped that the second edition will prove even better. *Wilder D. Bancroft*

Elektrische Spektralanalyse chemischer Atome. *By J. Stark. 16 × 23 cm; pp. iii + 138. Leipzig: S. Hirzel, 1914. Price: paper, 5 marks; cloth, 6 marks.*—When canal rays pass through a gas, we get rapidly moving particles, some of which are positively charged ions, some negatively charged ions and still others neutral atoms or molecules. The rates of motion of these three sets of particles will be affected differently by an electrical field. By studying the varying intensities of the spectral lines under these circumstances, one can draw conclusions as to the particles emitting certain spectral lines. The arc lines are believed, for instance, to be due generally to particles which contain at least one electron more than those to which the spark lines are due.

The author discusses the methods of experimenting and then takes up the theoretical side of the problem. The theoretical side would be more satisfactory if the author had considered the probability of light being due to a reaction and not necessarily to a particle. *Wilder D. Bancroft*

A Manual of Practical Physical Chemistry. *By Francis W. Gray. 19 × 14 cm; pp. xvi + 211. London: Macmillan and Co., 1914. Price: 4s. 6d.*—This little manual contains a series of thirty-nine exercises so arranged that each can be finished inside a normal laboratory period. The ground seems to be covered fairly well. The most striking novelty in the book is the use of the word "dissolecule" to mean molecular weight, p. 43. *Wilder D. Bancroft*

NAME INDEX

To Papers

NAME INDEX

To New Books

SUBJECT INDEX

Exclusive of New Books